Combustion chemistry of biodiesel for the use in urban transport buses: experiment and modeling

Hamid Omidvarborna

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entitled

Combustion Chemistry of Biodiesel for the Use in Urban Transport Buses: Experiment and Modeling

by

Hamid Omidvarborna

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the Doctor of Philosophy Degree in Engineering

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August 2016
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An Abstract of

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August 2016

Biofuels, such as biodiesel, offer benefits as a possible alternative to conventional fuels due to their fuel source sustainability and their reduced environmental impact. Before they can be used, it is essential to understand their combustion chemistry and emission characterizations due to a number of issues associated with them (e.g., high emission of nitrogen oxides (NOx), lower heating value than diesel, etc.). During this study, emission characterizations of different biodiesel blends (B0, B20, B50, and B100) were measured on three different feedstocks (soybean methyl ester (SME), tallow oil (TO), and waste cooking oil (WCO)) with various characteristics, while an ultra-low sulfur diesel (ULSD) was used as base fuel at low-temperature combustion (LTC).

A laboratory combustion chamber was used to analyze soot formation, NOx emissions, while real engine emissions were measured for further investigation on PM and NOx emissions. For further study, carbon emissions (CO, CO₂, and CH₄) were also measured to understand their relations with feedstocks’ type. The emissions were correlated with fuel’s characteristics, especially unsaturation degree (number of double bonds in methyl esters) and chain length (oxygen-to-carbon ratio). The experimental
results obtained from laboratory experiments were confirmed by field experiments (real engines) collected from Toledo area regional transit authority (TARTA) buses.

Combustion analysis results showed that the neat biodiesel fuels had longer ignition delays and lower ignition temperatures compared to ULSD at the tested condition. The results showed that biodiesel containing more unsaturated fatty acids emitted higher levels of NOx compared to biodiesel with more saturated fatty acids. A paired t-test on fuels showed that neat biodiesel fuels had significant reduction in the formation of NOx compared with ULSD. In another part of this study, biodiesel fuel with a high degree of unsaturation and high portion of long chains of methyl esters (SME) produced more CO and less CO₂ emissions than those with low degrees of unsaturation and short chain lengths (WCO and TO, respectively). In addition, biodiesel fuels with long and unsaturated chains released more CH₄ than the ones with shorter and less unsaturated chains.

Experimental results on soot particles showed a significant reduction in soot emissions when using biodiesel compared to ULSD. For neat biodiesel, no soot particles were observed from the combustion regardless of their feedstock origins. The overall morphology of soot particles showed that the average diameter of ULSD soot particles was greater than the average soot particle from biodiesel blends. Eight elements were detected as the marker metals in biodiesel soot particles. The conclusion suggests that selected characterization methods are valuable for studying the structure and distribution of particulates.

Experiments on both PM and NOx emissions were conducted on real engines in parallel with laboratory study. Field experiments using TARTA buses were performed on
buses equipped with/without post-treatment technologies. The performance of the bus that ran on blended biodiesel was found to be very similar to ULSD. As a part of this study, the toxic nature of engine exhausts under different idling conditions was studied. The results of the PM emission analysis showed that the PM mean value of emission is dependent on the engine operation conditions and fuel type. Besides, different idling modes were investigated with respect to organic carbon (OC), elemental carbon (EC), and elemental analysis of the PMs collected from public transit buses in Toledo, Ohio.

In the modeling portion of this work, a simplified model was developed by using artificial neural network (ANN) to predict NOx emissions from TARTA buses via engine parameters. ANN results showed that the developed ANN model was capable of predicting the NOx emissions of the tested engines with excellent correlation coefficients, while root mean square errors (RMSEs) were in acceptable ranges. The ANN study confirmed that ANN can provide an accurate and simple approach in the analysis of complex and multivariate problems, especially for idle engine NOx emissions.

Finally, in the last part of the modeling study, a biodiesel surrogate has been proposed and main pathways have been derived to present a simple model for NOx formation in biodiesel combustion via stochastic simulation algorithm (SSA). The main reaction pathways are obtained by simplifying the previously derived skeletal mechanisms, including saturated methyl decenoate (MD), unsaturated methyl 5-decanoate (MD5D), and n-decane (ND). ND is added to match the energy content and the C/H/O ratio of actual biodiesel fuel. The predicted results are in good agreement with a limited number of experimental data at LTC conditions for three different biodiesel fuels consisting of various ratios of unsaturated and saturated methyl esters. The SSA model
shows the potential to predict NOx emission concentrations, when the peak combustion temperature increases through the addition of ULSD to biodiesel. The SSA method demonstrates the possibility of reducing the computational complexity in biodiesel emissions modeling.

Based on these findings, it can be concluded that both alternative renewable fuels (biodiesel blends) as well as the LTC condition are suitable choices for existing diesel engines to improve the sustainability of fuel and to reduce environmental emissions.
Dedicated to the people who kept me going

when I wanted to give up

to my parents and my lovely wife
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List of Abbreviations

amu………………………atomic mass unit
ANN……………………Artificial Neural Network
ASTM…………………American Society for Testing and Materials

CH₄………………………Methane
CO………………………Carbon Monoxide
CO₂…………………Carbon Dioxide

EC …………………Elemental Carbon
EDX …………………Energy Dispersive X-ray
EGR…………………Exhaust Gas Recirculation

FAME …………………Fatty Acid Methyl Ester
FTIR …………………Fourier Transform Infrared Spectroscopy

GHG …………………Greenhouse Gas

HACA …………………Hydrogen Abstraction Carbon Addition
HC ……………………Hydrocarbon
HRTEM………………High-Resolution Transmission Electron Microscopy

ICP-MS ………………Inductively Coupled Plasma Mass Spectrometry
ICP-OES ………………Inductively Coupled Plasma Optical Emission Spectrometry
IV ………………………Iodine Value

LTC …………………Low-Temperature Combustion

MB ……………………Methyl Butanoate
MC ……………………Monte Carlo
MD ……………………Methyl Decanoate
MD5D …………………Methyl-5-Decanoate

ND ……………………Normal Decane
NOx …………………Nitrogen Oxides

OC ……………………Organic Carbon
PAH..........................Polycyclic Aromatic Hydrocarbon
PDHID ....................Pulsed Discharge Helium Ionization Detector
PM..........................Particulate Matter
PMF..........................Positive Matrix Factorization

SSA .........................Stochastic Simulation Algorithm
SEM ........................Scanning Electron Microscope
SME ........................Soybean Methyl Ester
SO$_2$ ........................Sulfur Dioxide
STD ..........................Standard Deviation

TARTA ......................Toledo Area Regional Transit Authority
TC ..........................Total Carbon
TEM ........................Transmission Electron Microscope
TGA ..........................Thermo-Gravimetric Analysis
TO ..........................Tallow Oil

ULSD .......................Ultra-Low Sulfur Diesel
USEPA ......................United States Environmental Protection Agency

VOC ..........................Volatile Organic Carbon

WCO .........................Waste Cooking Oil

XRD ..........................X-ray diffraction
Chapter One

Introduction

Environmental and health concerns related to particulate matter (PM), nitrogen oxides (NOx), and carbon emissions have gained increasing attention in the past few decades. PMs, emitted by different sources, have been examined with great interest due to their abundance in the atmosphere and the negative effects on human health (heart diseases, respiratory ailments, and carcinogenic effects). Children, the elderly, and those with existing heart or lung disease, asthma, or other respiratory problems, are most sensitive to the health effects of breathing fine particles. Children are more vulnerable to air pollution because they breathe 50 percent more air per pound of body weight than do adults (USEPA, 2003).

The physical and chemical characteristics of the particles affect human health as well as climate change. Diesel engines emit a complex mixture of air pollutants, composed of gaseous and solid material. The visible emissions in diesel exhaust are known as PM. In 1998, California identified diesel exhaust PM as a toxic air contaminant based on its potential to cause cancer, premature death, and other health problems. Diesel engines also contribute to fine PM (PM$_{2.5}$) air quality problems. Those most vulnerable are children whose lungs are still developing and the elderly who may have other serious
health problems. Overall, diesel engine emissions are responsible for the majority of known cancer risk from outdoor air pollutants in urban areas. In addition, diesel soot causes visibility reduction and is a potent global warmer. The most well-known contributors of PMs in urban areas which should be minimized are (Giordano et al., 2010):

- Road-traffic-related exhaust mainly from diesel engines.
- Stationary sources of primary particle formation, such as power plants, metal industries, mines, etc.
- Secondary particle formation due to atmospheric oxidation of sulfur dioxide (SO$_2$), NOx, and volatile organic carbons (VOCs). Natural components, such as sea salt, re-suspended soil, and dust are also known to contribute to secondary particle formation (Harrison et al., 2008).

This fact confirmed the size of PM as one of the essential characteristics of PM, which should be considered. The shape, size and concentration of the PMs have a direct relationship to the risk assessment for human health (USEPA, 2002). These fine and ultrafine particles have higher specific surface areas and toxic effects than coarse PMs. Because the deposition efficiency is related to the size of PMs, smaller PMs can easily be inhaled and deposited in the respiratory tract and alveolar region. As a result, they are more likely to cause respiratory diseases (Pope et al., 1995; McAughey, 1997; Voutsa and Samara, 2002).

As mentioned earlier, emission characteristics of diesel-powered vehicles are recognized as a major contributor to PM generation in urban area (Maricq et al., 2000; Kongtip et al., 2006). In the past few years, significant efforts have been taken to reduce
PM emissions from vehicles, either by replacing diesel with alternative fuels (such as biodiesel), or through engine modifications such as exhaust gas recirculation (EGR) and after treatment technologies (catalytic converters). Diesel PMs consist of an agglomeration of primary carbon particles and condensed organic compounds, sulfate, and metallic ash (Maricq, 2007).

Besides the lowering PMs during combustion of oxygenated fuels in engines, the formation of other pollutions (e.g., NOx, CO, CO₂, and CH₄) should be controlled as well. NOx is a generic term for the nitrogen oxides which is defined as the total concentration of NO and NO₂. NOx react with ammonia, moisture, and other compounds to form small particles. These small particles penetrate deeply into sensitive parts of the lungs and can cause or worsen respiratory disease, such as emphysema and bronchitis, and can aggravate existing heart disease, leading to increased hospital admissions and premature death. In addition, ozone is formed when NOx and VOCs react in the presence of heat and sunlight. Children, the elderly, people with lung diseases such as asthma, and people who work or exercise outside are at risk for adverse effects from ozone. These include reduction in lung function and increased respiratory symptoms as well as respiratory-related emergency department visits, hospital admissions, and possibly premature deaths (USEPA).

NOx molecules are formed whenever combustion occurs in the presence of nitrogen and at elevated temperatures. Therefore, lowering the combustion temperature will be helpful in NOx reduction. EGR, as a practical way of low-temperature combustion (LTC), in diesel combustion engines reduces emissions, especially NOx, by
lowering the peak combustion temperature and oxygen level in cylinder (Hountalas et al., 2008; Agarwal et al., 2011b).

The benefits of biodiesel on greenhouse gas (GHG) emissions are also significant, because CO₂, as a main compound in GHG emissions, released from biodiesel combustion is offset by the CO₂ captured by the plants from which biodiesel is produced.

CO can cause harmful health effects by reducing oxygen delivery to the body's organs (like the heart and brain) and tissues. At extremely high levels, CO can cause death. Exposure to CO can reduce the oxygen-carrying capacity of the blood. People with several types of heart disease already have a reduced capacity for pumping oxygenated blood to the heart, which can cause them to experience myocardial ischemia (reduced oxygen to the heart), often accompanied by chest pain (angina), when exercising or under increased stress. For these people, short-term CO exposure further affects their body’s already compromised ability to respond to the increased oxygen demands of exercise or exertion (USEPA). CH₄ in its gas form is an asphyxiant, which in high concentrations may displace the oxygen supply you need for breathing, especially in confined spaces. Decreased oxygen can cause suffocation and loss of consciousness. It can also cause headache, dizziness, weakness, nausea, vomiting, and loss of coordination. Skin contact with liquid methane can cause frostbite. Although CH₄ is not toxic, it has a global warming potential as reported by Environment Canada in 2011 (25 times higher than that of CO₂).

1.1 Biodiesel Fuel and its Characterization

Biodiesel has received considerable attention for its potential as an alternative source of fuel for the transportation sector. The consumption of biodiesel has increased
dramatically since early 2000, as biodiesel was considered ready-to-use renewable energy, providing a solution to decrease GHG emissions. It helps stabilize the price of fossil fuel and enhances energy security. For these reasons, biodiesel has gained prominence as an attractive fuel in recent years. It is expected that biodiesel will be used extensively in the future because it offers the following characteristics (Smaling, 2006; NREL, 2009):

- Renewable and non-petroleum-based.
- Lower GHG emissions.
- Less toxic and biodegradable.
- Lower emissions of PM, CO, hydrocarbons (HCs), and other air toxins.
- Minor (or no) modifications needed for traditional compression ignition engine

Some of the limitations of biodiesel include:

- Lower heating value (small number of carbon atoms compared with ultra-low sulfur diesel (ULSD)).
- Potentially high emissions of NOx.
- Variation in chemical properties due to differences in feedstock.
- High manufacturing cost.

Until recently, most biodiesel fuels were produced from plant oils, such as soybean oil (USA), rapeseed oil (EU), or palm oil (Asia). Recently the range of feedstocks has been extended to many other oils, fats, and waste oils. Today, biodiesel fuels are produced commercially from the following feedstocks (NREL, 2009):
• Animal fats: edible, inedible, and all other variations of tallow, lard, choice white grease, yellow grease, poultry fats, and fish oils.

• Plant oils: soy, corn, canola, sunflower, rapeseed, safflower, and cottonseed.

• Recycled oils and greases: waste cooking oils (WCOs), used motor oils, and greases.

The fats and oils typically used for biodiesel production are chemically similar and contain approximately 10 common types of fatty acids, each having 12 to 22 carbons in their molecular structure, more than 90% of which contain 16 to 18 carbons. Each feedstock is distinguished from the others by its unique proportions of saturated, monounsaturated, and polyunsaturated fatty acids (NREL, 2009).

The fatty acid compositions (unsaturation degree) of feedstock oils determine not only the properties of the fuel, but also its emission levels and characteristics. Other chemical components besides fatty acids also have different concentrations in biodiesel, depending on the type of feedstock and blends. Moreover, biodiesel contains about ten percent oxygen while regular diesel has no oxygen content in its constituent molecules. Therefore, combustion engines that use biodiesel fuels must be designed and operated accordingly to maximize engine efficiency and minimize emissions.

1.2 Biodiesel and PM

In several studies, environmental benefits associated with biodiesel were investigated, and biodiesel was regarded as a viable replacement for petroleum-based diesel fuels. The majority of these studies note that PMs produced from biodiesel was low in comparison with PM generated from regular diesel (Graboski and McCormick,
1998; Monyem and Van Gerpen, 2001; USEPA, 2002; Lapuerta et al., 2008; Tormos et al., 2010). In addition, biodiesel emitted less CO, unburned HCs and soot (solid carbon fraction of PM) mainly due to higher oxygen-to-carbon content than conventional fuels. Higher oxygen content leads to a complete combustion and, as a result, it helps reduce emissions too. In addition, the presence of oxygen during the formation process enhances soot oxidation which reduces PM mass and size distribution (Omidvarborna et al., 2015b).

1.3 Biodiesel and NOx Emissions

It is reported that biodiesel and its blends in general show higher NOx emissions (Szybist et al., 2005; Fernando et al., 2006; Hoekman et al., 2012). The main reason for the differences of NOx production between biodiesel and ULSD is reported to be due to the presence of high oxygen contents in biodiesel (Hoekman et al., 2012). Biodiesel has no nitrogen atoms in its constituent molecules, and thereby during the combustion, N₂ molecules from the air in the presence of extra oxygen molecules are converted to NOx at elevated temperatures. Therefore, burning fuels at lower temperatures help emission reduction. In addition, because of the lower heating value of biodiesel, more biodiesel should be burned to produce the equivalent energy. Thus, for the same heat generation, biodiesel may produce more emissions of NOx than regular diesel. Additionally, biodiesel fuel characteristics are thought to be important on NOx formation, when different feedstocks are considered. Due to its limitations, biodiesel is normally blended with ULSD by 20 percent or less in volume (Omidvarborna et al., 2014).
1.4 Biodiesel and Carbon Emissions

According to the USEPA, the majority of carbon emissions from the transportation sector are from CO$_2$ emissions and relatively small amounts of other components, e.g., CO and CH$_4$ resulting from the combustion of petroleum-based products (diesel and gasoline) in engines (Kumar et al., 2014). Although CH$_4$ is not toxic, it has a global warming potential as reported by Environment Canada in 2011 (25 times higher than that of CO$_2$). It is reported that the contribution of traffic emissions to the total CO$_2$ emissions is as high as 23% (GHG data, 2006).

The benefits of biodiesel on GHG emissions are especially significant, because CO$_2$, as a main compound in GHG emissions, released from biodiesel combustion is offset by the CO$_2$ captured by the plants from which biodiesel is produced (Barabas et al., 2010). Moreover, technological improvements in engines in the last decades have greatly reduced the carbon emissions (Omidvarborna et al., 2015b), however, the main energy consumption and CO$_2$ emissions have experienced a sustained increase mainly due to population growth. Therefore, advanced technologies such as LTC with the implementation of alternative fuels are currently under extensive research and development to reduce the emissions. In addition, advances in molecular biology research make it possible to improve the profile of biofuel feedstocks to enhance the fuel properties and emissions reduction (Durrett et al., 2008).

One of the most important issues in the promotion of biodiesel is the wide variety of biodiesel feedstock types that result in different characteristics of biodiesel such as combustion parameters and emission characteristics (Omidvarborna et al., 2015c; Omidvarborna et al., 2016a). Various numbers of double bonds and chain lengths
(oxygen-to-carbon ratio) were reported to affect the fuel properties, combustion and emissions (Monyem and Van Gerpen, 2001; Utlu and Koçak, 2008; Ozsezen et al., 2009; Benjumea et al., 2011). Therefore, biodiesel combustion mechanism is much more complex than diesel, not only because of the size of the fuel molecules, but also the additional reactions of oxygen-containing species.

1.5 Modeling Study

There are very few robust emission models for biodiesel fuels due to complication of combustion processes (Omidvarborna et al., 2015b). Thousands of interactions are involved in a combustion process, and it is extremely complicated to simulate all of them via a single model. For deep investigation of the biodiesel combustion process in real engines, an artificial neural network (ANN) model was developed to predict NOx emissions from the exhaust. ANN was implemented due to the large number of input variables collected from real experiments, while stochastic simulation algorithm (SSA) was developed based on simplified mechanisms and tracking selected species in the exhaust in laboratory study. Detail information and literature review regarding each method (ANN and SSA) are presented in the following chapters.

1.6 Motivation of the Study and Objectives

Although it is generally accepted that biodiesel contributes to the reduction of pollutants, biodiesel and its blends still need more intensive and systematic study for better control of emissions and engine performance. Biodiesel combustion emissions vary significantly depending on combustion conditions, blending percentage, and type of feedstocks. This study is performed to gain a better understanding of the interaction
between the stated parameters (feedstock, blend, and combustion conditions) and exhaust emissions by characterizing soot and analyzing NOx and carbon emissions from a variety of emission-source categories. Analytical data of biodiesel in this study can be used for new engine design, engine modification, and development of a robust and realistic biodiesel combustion model. The engine emissions data will be helpful in establishing environmental standards and regulations for biodiesel manufacturers, engine designers, manufacturers, and consumers. In brief, the objectives of the current study are as follows:

- To better understand PM, NOx and carbon formation mechanisms from combustion of diesel and biodiesel fuels.
- To physically and chemically characterize PM (from engine combustion) and soot particles (from laboratory experiments) emitted from various feedstocks and blends.
- To determine the conditions for minimizing emissions.
- To develop a database for combustion characteristics of biodiesel fuels and their blends with ULSD.
- To model biodiesel combustion emissions under simplified conditions.

The goals were achieved by experimentally comparing the emissions of biodiesel from different feedstocks and blends under LTC. The exhaust gases were analyzed for NOx, CO, CO₂, CH₄ and produced PM and soot particles were collected for further experiments. Physical characterization of single soot particle can reveal source information, something that bulk chemical characterization, such as atomic absorption spectroscopy or X-ray fluorescence, cannot reveal. For chemical characterization of soot,
the collected soot samples from the combustion chamber were analyzed by using inductively coupled plasma mass spectrometry (ICP-MS) for their possible elements. For further analyses on forming soot particles, scanning electron microscope (SEM), transmission electron microscope (TEM), and Fourier transform infrared spectroscopy (FTIR) analyses were used to investigate the shape, size distribution and molecular structure of collected samples. Collecting samples from transit buses running on biodiesel blend was characterized to strengthen the findings too.

ANN and SSA approach were used to comprehensively understand the modeling capability of the algorithms for predicting the experimental data in complex conditions. NOx emissions from engines were simulated through ANN to analyze the emission characteristics of engines running on biodiesel blend in real systems. It is expected that the ANN modeling will help us to solve complex mechanism of engine emissions and to help modify the biodiesel emission standard as it will help reduce emissions. The low complexity of the simplified reaction mechanism enables it to be integrated into the SSA model to simulate the combustion characteristics. Therefore, the SSA method used in this study demonstrates the possibility of reducing the computational complexity in biodiesel emissions modeling. The specific goals are described in greater details in the following chapters.

1.7 Outline of the Thesis

Due to the complex mechanism of soot formation, detailed literature on soot formation and possible reactions is discussed. This is because an understanding of soot formation mechanisms is necessary for the study of soot particles, PM and their modeling. Chapter two reviews soot formations and oxidation mechanisms which will be
helpful to understand the nature of soot particles. This review shows how soot inceptions form and how much difference they have during and after formation in both diesel and biodiesel fuels.

In chapter three, the state-of-the-art laboratories for conducting the experimental observations are explained. Moreover, this chapter explores the mechanism and structure of forming NOx and soot particles in addition to carbon emissions from different feedstocks and blends with ULSD. Various analytical instruments were used to completely identify the nature of soot particles in this section. Formation and characteristics of NOx, soot particles, CO, CO$_2$, and CH$_4$ were compared from blend to blend as well as from feedstock to feedstock.

The databases on particle characterization were created using data collected through various stages of the project by using transit buses. Preliminary data for route and fuel was collected all along the sampling, which was conducted according to the convenience of all the concerned individuals. Chapter four provides a qualitative evaluation of the particles emitted from transit buses. This chapter underlines the particulate chemical characteristic from the exhaust and establishes carbon speciation and elemental emissions for the exhaust particles. Both chapter three and four give a reasonable view on the effects of engine parameters, combustion variables, and fuel characteristics on emissions and their specifications.

Chapter five and six are an attempt to model the exhaust emissions, especially NOx with the help of simple and practical models (ANN and SSA, respectively). Chapter seven covers the conclusions of all the chapters collectively and suggests future work.
Lists of all journal and conference papers published so far are presented in this chapter too. A schematic figure that represents the flow of this study is presented in Figure 1.1.

Figure 1.1. Integrated flow diagram showing relationship between different activities will be carried out during the study.
Chapter Two

Soot Formation Mechanism

In this chapter, five common steps appeared in soot formation mechanism in the literature were reviewed. In recent years particular attention has been paid to the reduction of soot from diesel combustion, because of the rising environmental and health concerns on soot particles that are found to be turned into mutagenic and potentially carcinogenic PMs. Other models and the related equations were discussed and compared with one another. The role of soot precursors and its implementation into modeling are the main focuses in reviewing the recent soot models to substantiate the issue of determining the species between acetylene and aromatic rings that play more dominant role in soot formation.\(^1\)

2.1 Background

The call for emission reduction has been mandated by many governments. For past few years, it has been one of the top priorities for combustion research centers to investigate combustion processes and emission reduction methods through optimizing the engines and fuels (Enweremadu and Rutto, 2010; Xue et al., 2011; Shahabuddin et al.,

\(^1\) The content of this chapter is published as a review paper entitled as: Omidvarborna, H., Kumar, A., and Kim, D.S. (2015b). Recent studies on soot modeling for diesel combustion, Renewable and Sustainable Energy Reviews 48, 635 - 47.
Soot modeling is regarded as an important part of understanding the process of soot formation, which in turn contributes to the development of effective emissions reduction techniques.

Diesel is known as a source of emission species such as PM, polycyclic aromatic hydrocarbons (PAHs), heavy metals, and NOx (Kunzli et al., 2000; Krzyzanowski et al., 2005). These species are produced from combustion and found in emissions mainly in the form of aerosols, and are recognized as health hazards (Kaden et al., 1979; Durant et al., 1996). Among these diesel emission components, PM has been a serious concern for human health due to its direct and broad impact on the respiratory organs (Kunzli et al., 2000; Krzyzanowski et al., 2005). In earlier times, health professionals associated PM$_{10}$ (diameter < 10 µm) with chronic lung disease, lung cancer, influenza, asthma, and the cause of increased mortality rate (Stöber and Abel, 1996). However, recent scientific studies suggest that these correlations be more closely linked with fine particles (PM$_{2.5}$) and ultra-fine particles (PM$_{0.1}$) (Schwartz, 1994), because the fine and ultra-fine particles can easily penetrate deep into the lungs. To address these problems, a great deal of air quality research has been performed on toxicity and chemistry of PM over the last 40 years (Mauderly, 1994; Salvi et al., 1999). It is generally reported that the majority of PM is originated from soot, (highly carbonaceous material which weighs typically higher than 50% in PM mass), which is usually formed in fuel-rich or low-oxygen regions of a diesel engine (Shandilya and Kumar, 2013; Kumar et al., 2014; Omidvarborna et al., 2014).

A better understanding of the soot formation made it possible to formulate mathematical models that predict the concentration or mass of soot in the emissions, and validate the proposed mechanisms, and in turn good models are helpful in better
understanding soot characteristics and formation mechanisms. Significant advances have been made on the mechanisms of soot formation in the last two decades (Haynes and Wagner, 1981; Bockhorn, 1994; Richter and Howard, 2000; Stanmore et al., 2001). However, it appears that there is still a gap between the existing soot models and actual soot formation processes. The gap becomes even greater when it comes to soot formation from combustion of oxygenated fuels (biodiesel fuels) due to the varying compositions and diverse types of feedstock (Murugesan et al., 2009; Misra and Murthy, 2011; Kumar et al., 2013).

2.2 Objectives

Soot modeling can be improved as long as the formation and oxidation mechanisms are clearly understood and, accordingly, more realistic assumptions are made. This review begins with a complete description of soot formation mechanism and summarizes the progress of soot modeling for diesel combustion. It is followed by different modeling approaches and comparison of those approaches along with the highlights of theoretical and empirical results.

2.3 Soot Structure

To better understand the mechanisms of soot formation found in the literature, it is worthwhile to briefly review the chemistry of the soot. Soot is a solid substance consisting of roughly eight parts of carbon and one part hydrogen (soot density is 1.847 g/cm³ (Choi et al., 1994) and the reports by most other authors fall near this value). In urban areas soot is mostly formed as a result of fuel combustion in engines and its characteristics do not appear to be functions of fuel and other operating conditions.
Soot becomes a part of black carbon/smoke when present in sufficiently large particle size and quantity in exhaust gases. Soot nucleates from the vapor phase to a solid phase in fuel-rich regions at elevated temperatures. HCs or other available molecules may condense on, or be absorbed by soot depending on the surrounding conditions (Tree and Svensson, 2007).

A newly formed soot particle initially has the highest hydrogen content, and the carbon-to-hydrogen ratio is as low as one. However, as the soot matures, the carbon fraction increases. Trace amounts of zinc, phosphorus, calcium, iron, silicon, and chromium are also often detected in emitted soot from diesel engines (Xi and Zhong, 2006; Shandilya et al., 2013; Omidvarborna et al., 2014; Omidvarborna et al., 2015a).

Soot is found to be in the size of sub-microns and in the form of necklace-like agglomerates (Haynes and Wagner, 1981). Figure 2.1(a) is a typical SEM image of diesel soot showing these agglomerates are composed of collections of smaller particle units in spherical or close to spherical shape (Bockhorn, 1994). X-ray diffraction (XRD), as illustrated in Figure 2.1(b) (Glassman, 1996), indicates that the carbon atoms of a primary soot particle are packed into hexagonal face-centered arrays, commonly referred to as platelets. Platelets are arranged in layers to form crystallites, and there are typically two to five platelets per crystallite (Glassman, 1996). When analyzed under high-resolution transmission electron microscopy (HRTEM), two distinct parts of a primary diesel soot particle can be identified: an outer shell and an inner core, as shown in Figure 2.1(c) (Ishiguro et al., 1997). The platelet model mentioned above applies to the outer shell. However, the inner core contains fine particles with a spherical nucleus surrounded by carbon networks with a bending structure. It shows that the outer shell, which is
composed of graphitic crystallites, is of a rigid structure, while the inner core is chemically and structurally less stable due to the thermodynamic instability of its structure. Arrangements of crystallites which contain inner/outer shells and fine particles in collected soot (with different sizes observed under HRTEM analysis) are shown in Figure 2.1(c).

Figure 2.1. (a) SEM image of soot aggregates in diesel exhaust collected from a Toledo area regional transit authority (TARTA) bus (b) Substructure of a soot particle (c1) Microstructure of diesel soot particles (Xi and Zhong, 2006) (c2) HRTEM image of collected soot from a combustion chamber.

In summary, the formation of soot, e.g., the conversion of HC fuel molecules into carbonaceous agglomerates, is an extremely complicated process. It is a kind of gaseous-
solid phase transition where the solid phase exhibits no unique physical and chemical structures, and the transition occurs through various chemical reaction and physical interaction steps. A number of approaches to soot modeling exist, but there is a trade-off between the capability of predicting the details of soot formation and computational time. Another issue in soot formation modeling is the complexity of simultaneous chemical and physical phenomena, such as precursor formation from the gas phase chemistry, primary particle inception, nucleation, particle growth, coagulation and particle oxidation which are hard to describe in a series of mathematical formula. So, simplified soot models that can produce more realistic results in reduced computational time are highly desired for engine design and emission control.

2.4 Soot Formation

The formation of soot is a complex process, an evolution of matter in which a number of molecules undergo many chemical and physical reactions within a few milliseconds. It is still not clearly understood how soot particles and their precursors are formed despite the broad and extensive studies published in the literature (Haynes and Wagner, 1981; Glassman, 1989; Bockhorn, 1994; Glassman, 1996). Many details of soot formation chemistry remain unanswered and controversial, but there have been a few agreements which are summarized here (Richter and Howard, 2000):

- Soot begins with some precursors or building blocks.
- Nucleation of heavy molecules occurs to form particles.
- Surface growth of a particle proceeds by adsorption of gas phase molecules.
- Coagulation happens via reactive particle-particle collisions.
- Oxidation of the molecules and soot particles reduces soot formation.
Many references proposed various soot formation processes in which many of them have in common. These widely agreed mechanisms proceed in three steps and are depicted in Figure 2.2. Large aromatic rings are formed mainly through addition of light HCs (acetylene) molecules in the molecular scale. Primary soot particles are supposed to be formed either by surface growth or coagulation of these larger aromatic compounds.

![Diagram of soot formation](image)

Figure 2.2. A conceptual description of progression of soot formation in three steps (Bockhorn, 1994).

### 2.4.1 Precursors for Soot Formation

The species that are considered to be the onset for soot formation and growth are referred to as precursors. Soot inception is a mechanism through which the precursors are resulted from fuel combustion to form soot particles. Inception is poorly understood because the nascent soot particles are extremely small (about 1 nm in diameter) thus making experimental investigations is very difficult (Richter and Howard, 2000). Among them acetylene has received great attention (Kong et al., 2007). Acetylene has been
identified by Glassman (1989) and later confirmed by Richter and Howard (2000) as a very important precursor for soot formation in diesel combustion, most likely because the first aromatic rings are formed from C2 and C3 additions (Miller and Melius, 1992).

In 1990s, Frenklach and Wang (1994) proposed that the addition of acetylenes lead to the formation of first aromatic rings, and those aromatic rings are the soot precursors. Due to limited formation of some intermediate molecules via acetylene and complexity of experimental studies, PAHs molecules instead of acetylene are much more considered as soot precursor in diesel combustion (Richter et al., 2000; Vishwanathan and Reitz, 2009). PAH formation and its growth appear to depend mainly on the type of fuel. Some of the reaction sequences which depict the formation of first aromatic rings are summarized elsewhere (Xi and Zhong, 2006).

2.4.2 Nucleation
The next step, nucleation or inception of particles from heavy PAH molecules, bridges the transition from gaseous media in a combustion process to heavy molecules that eventually turn into nascent soot. The molecular mass of nascent soot is approximately 2000 atomic mass unit (amu) (Haynes and Wagner, 1981) with an effective diameter of about 1.5 nm (can be detected by HRTEM) (Richter and Howard, 2000), while it is commonly believed that nucleation starts at lower amu around 300–700 (Frenklach and Ebert, 1988).

2.4.3 Mass Growth
Soot surface growth is the overall mechanism through which soot particle masses grow via the addition of gas species such as acetylene and PAH molecules/radicals. There is no clear distinction between the end of the nucleation and the beginning of surface growth and in reality the two processes are concurrent. Frenklach et al. (1985, 1988)
introduced the surface growth reaction mechanism back in 1980s. Soot particles undergo surface reactions with gaseous species via the hydrogen abstraction carbon addition (HACA) process (Frenklach, 2002; Frenklach and Wang, 1994). For HACA growth, the soot surface property is an important factor in soot mass growth. C-H bonds on the surface of the soot interfere with H and OH radicals to form reactive sites, where gaseous molecules (particularly acetylene) can be added to the surface of the soot particle (Frenklach, 2002; Harris and Weiner, 1983).

2.4.4 Coagulation
As depicted in Figures 2.2, during nucleation, particle growth happens through the coagulation step, e.g., a combination of two or more particles to form a larger particle, sometimes called coalescence (Bockhorn, 1994; Tree and Svensson, 2007). The results of experiments depict that particle coagulation process occurs almost immediately after the soot particle formation, or when soot particles are relatively small or young (Bockhorn, 1994). Sticking collisions between particles during the mass growth process significantly increase the particle size and decrease the number of particles without changing the total mass of soot present. Sometimes individual or primary particles stick together to form large groups of primary particles which maintain their shape. In this case the process is called agglomeration. So, the coagulation process forms a large particle by combining small particles, where during agglomeration the primary particles stick to each other, forming a group of chain-like aggregates. An example of agglomeration is easily found in the collection of exhaust soot from a diesel engine. In soot exhaust, soot consists of primary particles which are spherical in shape, and they are agglomerated to form long chain-like structures as shown in Figure 2.1(a).
2.4.5 Oxidation Process

Soot oxidation is the result of the processes that reduce the mass of soot by converting the solid soot particles or part of them back into gases (e.g., CO and carbon dioxide or CO$_2$). Oxidation is similar to the surface growth in a sense that the surface area of the particles affects the rate of oxidation. Oxidation takes place on the surfaces of soot particles and decreases the mass of soot and reduces the mass of carbon accumulated in the soot particles (Bockhorn, 1994). Unlike the surface growth of soot, which occurs in a specific step, oxidation happens all the time during and after soot formation. Oxidizing elements are O, O$_2$, and OH under fuel-rich conditions, but in fuel-lean media H$_2$O, CO$_2$, NO, N$_2$O, and NO$_2$ are also possible oxidants (Stanmore et al., 2001). More oxidation models in which oxidants other than O$_2$ are involved are presented elsewhere (Nagle and Strickland-Constable, 1962; Stanmore et al., 2001).

A comprehensive review for the fundamentals of soot formation mechanism is beyond the scope of this chapter. More in-depth reviews were provided by earlier studies (Haynes and Wagner, 1981; Glassman, 1989; Bockhorn, 1994; Glassman, 1996).

2.5 Soot Models

Soot mechanism is difficult to model mathematically because of the large number of primary components of diesel fuel, quite complex combustion mechanisms, and the heterogeneous interactions during soot formation (Belardini et al., 1996). Soot models are broadly categorized into three subgroups (Kennedy, 1997). Empirical (equations that are adjusted to match experimental soot profiles), semi-empirical (combined mathematical equations and some empirical models which used for particle number density and soot volume and mass fraction), and detailed theoretical mechanisms (covers detailed
chemical kinetics and physical models in all phases) are usually available in literatures for soot models.

Such comprehensive models (detailed models) usually take high financial burden for programing and operating, and much computational time to produce a converged solution. On the other hand, empirical and semi-empirical models ignore some of the details in order to make complex model simple and to reduce the computational cost and time. Thanks to recent technological progress in computation, it becomes more feasible to use detailed theoretical models and obtain more realistic results. However, further advancement of comprehensive theoretical models must be preceded by the more detailed and accurate formation mechanisms. On the other hand, models that are based on a phenomenological description have found wide use recently. Phenomenological soot models, which may be categorized as semi-empirical models, correlate empirically observed phenomena in a way that is consistent with the fundamental theory, but is not directly derived from the theory. Phenomenological models use sub-models developed to describe the different processes (or phenomena) observed during the combustion process. These sub-models can be empirically developed from observation or by using basic physical and chemical relations. Advantages of phenomenological models are that they are quite reliable and yet not so complicated. So, they are useful, especially when the accuracy of the model parameters is low. Examples of sub-models of phenomenological empirical models could be listed as spray model, lift-off model, heat release model, ignition delay model, etc.
2.6 Conclusion

Fundamental concepts and models about soot mechanism in diesel and biodiesel combustion emissions are examined in this review paper. Fuel combustion process is very complex, and their detailed mechanisms on soot are not quite well understood. From the literature review, it can be observed that the emission of soot from the biodiesel-fueled engine is less than ULSD. However, more experimental and theoretical studies are needed to describe the complicated process of soot mechanisms in biodiesel combustion.

Soot formation and oxidation steps were incorporated in early studies on soot mechanism. Later on, due to emerging new computational systems along with modern experimental and analytical tools, common steps in soot mechanism were identified. Following these steps results in more accurate results compared to experimental data as described earlier. Among the proposed models for different combustion systems, empirical and semi-empirical soot models are found relatively simple and practical for specific systems where experimental results have been implemented into the models. In recent years, phenomenological models have been found to be more effective tool for simple and easy prediction of soot mechanism, but case by case adjustment of the implemented parameters may be needed. Detailed models were introduced as the most accurate and comprehensive models. These models require a great deal of computational time and cost. It is concluded that modeling of acetylene and its isomers as a starting component for formation of soot precursors seems to be a reasonable approach to the diesel soot modeling. The size of the model is important in determining the amount of computational time in detailed models, because the rate of soot precursor formation for each fuel will be dependent on fuel structure.
Regarding soot formation in biodiesel combustion, simple molecules such as methyl butanoate (MB), methyl decanoate (MD), and n-heptane were identified as common fuel surrogates in modeling. The degrees of oxygenation and saturation (e.g., the number of double bonds) of biodiesel fuels appear to be the important factors to be included in biodiesel soot modeling. This is because of the number and position of double bonds which may affect the reaction pathways and mechanisms. For the biodiesel soot modeling, due to lower emission of PAHs, the oxidation of precursors such as PAHs may be excluded. On the other hand the effect of early CO$_2$ production in biodiesel combustion on soot formation should be considered. Modeling of soot formation has to address all these aspects of regular and biodiesel combustions. In order to develop more robust and reliable models for soot formation, it is recommended that more reasonable assumptions be made based on a better understanding of chemical and physical interactions in soot mechanism. A fundamental challenge in soot modeling for biodiesel is the inability to predict differences in soot formation for different feedstock types and their blends with regular diesel. Further research needs to be carried out to understand the relationship between the type of biodiesel feedstock and performance and emission.
Chapter Three

Laboratory Experiments, Emission Analysis

Biodiesel has become important in transportation sectors due to its environmental benefits and the recent increase in energy demand. This chapter investigates the effects of neat biodiesel fuels and their blends with regular diesel on combustion characteristics and exhaust emissions at LTC. LTC looks to put diesel back on the menu for environmental solutions. Therefore, in this chapter, experiments were performed to better understand the effects of the combustion parameters such as degree of unsaturation, ignition delay, and ignition temperature on the NOx and carbon emissions (CO, CO$_2$, and CH$_4$) as well as soot formation of selected fuels. In addition, the morphology, microstructure, and sizes of soot particles were investigated to determine their relations with soot formation and oxidation processes$^1$.

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$^1$ The contents of this chapter are published (submitted) as three papers entitled as:
3.1 Introduction

Biodiesel and its blends in general are known to produce lower CO and HC emissions and higher NOx emissions compared with regular diesel (Szybist et al., 2005; Demirbas, 2007; Robbins et al., 2011; Omidvarborna et al., 2014; Kumar et al., 2014; Omidvarborna et al., 2015a; Omidvarborna et al., 2015b). In this chapter formation of NOx, CO, CO₂, CH₄ and soot from biodiesel fuels with various feedstocks and blends were investigated under LTC.

3.1.1 NOx Emissions

The reduction of NOx emissions is one of the most important technical challenges facing biodiesel, especially in light of the increasingly stringent exhaust emissions regulations on diesel engines (Knothe et al., 2006). NOx formation during biodiesel combustion is associated with a number of factors such as the property of biodiesel and combustion conditions. It has been reported that combustion temperature has great impact on NOx emissions (Hoekman and Robbins, 2012; Omidvarborna et al., 2014; Kumar et al., 2014). Low-temperature may help thermal NOx be reduced during combustion that led to LTC technology (Hill and Smoot, 2000; Varatharajan and Cheralathan, 2012).

3.1.2 Soot Emissions

In recent years particular attention has been paid to the reduction of soot from diesel combustion, because of the rising environmental and health concerns on soot particles that are found to be turned into mutagenic and potentially carcinogenic PMs (Omidvarborna et al., 2014; Kumar et al., 2014; Shandilya and Kumar, 2014; Omidvarborna et al., 2015b). Soot consists of carbonaceous material accompanied by various organic and inorganic compounds (Shandilya and Kumar, 2014; Omidvarborna et
al., 2014). Biodiesel lacks sulfur and aromatics, which are considered to be critical for the nucleation step and initial formation of PAHs leading to soot (Song et al., 2006; Lapuerta et al., 2008; Vander Wal et al., 2010; Salamanca et al., 2012b; Kumar et al., 2014). From the chemical point of view, unsaturation and high oxygen contents in biodiesel are thought to contribute to the reduction of soot too (Kohse-Höinghaus et al., 2010).

3.1.3 Carbon Emissions

Being a renewable and sustainable source of fuel, biodiesel will play a dominant role in the transportation sector in the near future, but, the choice of feedstock for biodiesel production depends on the status of domestic sources. Biodiesel has received considerable attention for its potential in the transportation sector, where it offers advantages on tailpipe emissions over ULSD. As mentioned earlier, the majority of carbon emissions from the transportation sector consist of CO$_2$ emissions and relatively small amounts of other components, e.g., CO and CH$_4$. Although CH$_4$ is not toxic, it has a global warming potential as reported by Environment Canada in 2011 (25 times higher than that of CO$_2$). It is reported that the contribution of traffic emissions to the total CO$_2$ emissions is as high as 23% (GHG Data, 2006). Moreover, the benefits of biodiesel on GHG emissions are especially significant, because CO$_2$, as a main compound in GHG emissions, released from biodiesel combustion is offset by the CO$_2$ captured by the plants from which biodiesel is produced (Barabas et al., 2010). Although technological improvements in engines in the last decades have greatly reduced the carbon emissions (Omidvarborna et al., 2015b), the main energy consumption and CO$_2$ emissions have experienced a sustained increase mainly due to population growth.
3.2 Objectives

3.2.1 NOx Emissions
Although no single theory provides an adequate explanation on the relations between biodiesel properties and NOx emissions under various conditions, it has been suggested that the degree of unsaturation of biodiesel play an important role in NOx formation during combustion (Lapuerta et al., 2009; Benjumea et al., 2011). The main goal of this part is to better understand the effect of unsaturation on the combustion parameters of biodiesel from different feedstocks under LTC (including ignition temperature, ignition delay, and NOx emissions). Experiments were conducted on a laboratory combustion chamber fueled with three different types of biodiesel and their blends with ULSD. In the first part, the chemical characteristics of biodiesel samples were discussed and compared with those of ULSD. Molecular structures of various biodiesel feedstocks were analyzed using FTIR mainly for their unsaturation. Then, the effects of defined combustion parameters were investigated. NOx emissions from the blends of the biodiesel samples were compared to each other to determine the samples that most significantly reduced NOx emissions. Paired t-test was used to statistically assess the difference in the effects of NOx emissions from the pair of fuels (Mccormick et al., 2001; EPA, 2002; Holden et al., 2006; Anderson, 2012).

3.2.2 Soot Emissions
As mentioned earlier, the type and proportion of the fatty acid molecules are thought to be the most-important factors that affect fuel emissions. In addition, the number of double bonds (e.g., the degree of unsaturation) was hypothesized to play an important role in soot formation too (Benjumea et al., 2011; Salamanca et al., 2012b). The actual diesel soot formation process is very complex and associated with engine
operation and environmental conditions as well as fuel structure and composition (Neer and Koylu, 2006; Lapuerta et al., 2008; Lin et al., 2008; Cengiz and Sehmus, 2009; Gogoi and Baruah, 2011; Muralidharan and Vasudevan, 2011). Therefore, it is reasonable to speculate that soot characteristics obtained from a diesel engine would represent fuels’ chemical specifications. In addition, there is a lack of knowledge if the biodiesel from other feedstocks would alter the detailed physical and chemical properties of the soot particles.

This part investigates the properties of soot from the combustion of different biodiesel derived from various feedstocks. The detailed morphological, structural and compositional features thus revealed would allow a much improved understanding of the characteristics of soot, providing a thorough assessment of the influence of biodiesel fuel structure on soot characteristics. FTIR, ICP-MS, thermo-gravimetric analysis (TGA), and TEM were used to analyze the unsaturation of biodiesel fuels and the morphology of soot. The information will be helpful in selecting the appropriate blends for mobile sources used around the globe and also provide insights into the mechanisms of the fuel formulation in diesel combustion and soot formation processes.

3.2.3 Carbon Emissions

Reductions in total HCs and CO emissions with an increase of biodiesel chain length has been reported (Knothe et al., 2006; Schönborn et al., 2009). Although many researchers have looked into the impact of biodiesel on NOx emissions, few have discussed the effect of fatty acid compositions on the properties of carbon emission components, and no clear conclusion concerning the unsaturation degree of fatty acids has been reached (McCormick et al., 2001; Knothe et al., 2006; Schönborn et al., 2009; Benjumea et al., 2011; Pinzi et al., 2013). The two of the most important characteristics
that determine the biodiesel properties are the chain length and the degree of unsaturation of fatty acid methyl esters (FAMEs). This section compared biodiesel fuels derived from different feedstocks for their carbon emission characteristics under the LTC conditions. Biodiesel derived from soybean methyl ester (SME), WCO, and tallow oil (TO), were used, whose chain lengths and degrees of unsaturation were different. These biodiesel fuels and their blends with ULSD were combusted in a laboratory combustion chamber and the compositions of emissions were analyzed. This study gives valuable knowledge on the combustion characteristics, fuel properties and carbon emissions of three common kinds of biodiesel feedstocks under fuel-rich LTC conditions.

3.3 Experimental Setup and Procedure

3.3.1 Fuels Specification

Biodiesel defined by ASTM D6571 is a non-petroleum-based diesel fuel which is made by transesterification of mono-alkyl esters of fatty acids from vegetable oils and animal fats. Most commercial biodiesel fuels are mainly composed of natural medium to long-chain FAMEs. An essential characteristic of biodiesel fuels is that its fatty acid profile corresponds to its principal oil or fat. The main structural features of fatty acids are their chain length and the number of double bonds.

The major fatty acid structures and compositions for neat biodiesel samples used in this study are presented in Table 3.1 and plotted in Figure 3.1. As shown in Figure 3.1, oleic acid (C18:1), linoleic acid (C18:2), and linolenic acid (C18:3) have 18 carbon atoms and 1, 2, or 3 double bonds in their structure, respectively.
The degree of unsaturation of a FAME molecule depends on the number of double bonds present in its fatty acid chain. The high numbers of double bonds represent high degrees of unsaturation (Benjumea et al., 2011). As shown in Table 3.1, SME is the most unsaturated fuel with significant contents of mono-unsaturated (22.8% C18:1), di-unsaturated (53.7% C18:2) and tri-unsaturated (8.6% C18:3) fatty acids. Compared with SME, WCO is medium unsaturated with 52.9% of mono-unsaturated and 13.5% of di-unsaturated fatty acid. TO is the least unsaturated with only 42.4% of mono-unsaturated fatty acid. Due to the presence of mostly 18-carbon saturated and unsaturated chains in FAMEs, the effects of chain lengths on combustion parameters and NOx emissions are considered insignificant compared to the degree of unsaturation. For pure FAMEs, the oxygen content increases slightly with the degree of unsaturation because of the displacement of two hydrogen atoms by saturation of double bonds (Benjumea et al., 2011).

Table 3.1. Major fatty acid composition of the feedstocks in mass percent

<table>
<thead>
<tr>
<th>FAMEs</th>
<th>Chemical Formula</th>
<th>Chemical Structure a</th>
<th>C:H Ratio</th>
<th>C:O Ratio</th>
<th>SME</th>
<th>WCO</th>
<th>TO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric</td>
<td>C_{12}H_{24}O_2</td>
<td>C12:0</td>
<td>1:2</td>
<td>6:1</td>
<td>0.1</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Myristic</td>
<td>C_{14}H_{28}O_2</td>
<td>C14:0</td>
<td>1:2</td>
<td>7:1</td>
<td>0.1</td>
<td>0.9</td>
<td>2.8</td>
</tr>
<tr>
<td>Palmitic</td>
<td>C_{16}H_{34}O_2</td>
<td>C16:0</td>
<td>~1:2.1</td>
<td>8:1</td>
<td>10.2</td>
<td>20.4</td>
<td>23.3</td>
</tr>
<tr>
<td>Stearic</td>
<td>C_{18}H_{36}O_2</td>
<td>C18:0</td>
<td>~1:2.1</td>
<td>9:1</td>
<td>3.7</td>
<td>4.8</td>
<td>19.4</td>
</tr>
<tr>
<td>Oleic</td>
<td>C_{18}H_{36}O_2</td>
<td>C18:1</td>
<td>1:2</td>
<td>9:1</td>
<td>22.8</td>
<td>52.9</td>
<td>42.4</td>
</tr>
<tr>
<td>Linoleic</td>
<td>C_{18}H_{36}O_2</td>
<td>C18:2</td>
<td>~1:1.9</td>
<td>9:1</td>
<td>53.7</td>
<td>13.5</td>
<td>2.9</td>
</tr>
<tr>
<td>Linolenic</td>
<td>C_{18}H_{36}O_2</td>
<td>C18:3</td>
<td>~1:1.8</td>
<td>9:1</td>
<td>8.6</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>C16:0 and lower</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10.4</td>
<td>21.3</td>
<td>26.2</td>
</tr>
<tr>
<td>C18:0 ≥</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>88.8</td>
<td>72.0</td>
<td>65.6</td>
</tr>
<tr>
<td>Total saturated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>14.1</td>
<td>26.1</td>
<td>45.6</td>
</tr>
<tr>
<td>Total Unsaturated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>85.1</td>
<td>67.2</td>
<td>46.2</td>
</tr>
</tbody>
</table>

* C18:0 describes a molecule with a chain of 18 carbon atoms and 0 double bonds.
Note: C:O ratio for SMEB20 is reported as 45:1 (DeOliveira et al., 2006).

The compositions of the main components (carbon, oxygen and hydrogen) were calculated in terms of the weight percent of each element for the feedstock as presented
in Table 3.1. Based on molecular weights and mass fractions provided in Table 3.1, the C/O/H ratios for SME, WCO, and TO were calculated as 76.2/11.4/12.4, 75.7/11.5/12.8, and 75.4/11.6/13.0, respectively. Therefore, SME contains the highest fraction of carbon atom, whereas TO contains the highest fraction of oxygen atom. Carbon-to-oxygen ratios for SME, WCO, and TO were 6.7, 6.6, and 6.5, respectively. Therefore, for the conditions used in the tests, short chain saturated methyl esters such as TO provide suitable conditions for more complete combustion. Besides, the fuel’s properties confirmed that the degree of unsaturation increases as the chain lengths increases in the selected biodiesel fuels.

![Fatty Acid Molecules](image_url)

Figure 3.1. Seven fatty acid molecules commonly found in biodiesel (Herbinet et al., 2008; Lai et al., 2011).

In the first step, the test samples were grouped into three blends (B20, B50, and B100) of three different biodiesel feedstocks (SME, TO, WCO). ULSD (as a base fuel) and SME were obtained from TARTA Company (purchased from Peter Cremer), TO obtained from United Oil Inc. (Pittsburgh, PA), and WCO obtained from White Mountain
Biodiesel (North Haverhill, NH). These fuels and their blends with ULSD are tested for combustion and emissions analysis in a laboratory combustion chamber with particular emphasis upon NOx emissions.

FTIR spectroscopy has been commonly implemented as a useful tool in biodiesel analysis due to its reproducibility, accuracy, and simplicity (Bouaid et al., 2007; Jain and Sharma, 2011; Zhang, 2012; Issariyakul and Dalai, 2014). The FTIR spectra of all the fuel samples were obtained using a Varian FTIR spectrometer in a scanning mid-IR range of 650 to 4000 cm\(^{-1}\).

Figure 3.2(a) shows the FTIR spectra of neat fuel samples used in this study and represents an overview of spectra for different components. The major parts of the spectra in Figure 3.2(a) are explained in Figure 3.2(b–d) in more detail. As shown in Figure 3.2(b), ULSD showed no significant peaks in the range of single bonds (1150 to 1550 cm\(^{-1}\)). Two peaks of ULSD at 1370 and 1452 cm\(^{-1}\) represent alkyl bonds, methyl and methylene, respectively. Biodiesel peaks at 1160, 1190, 1245 and 1375 cm\(^{-1}\) represent C-O bonds, especially esters within the range of single bonds at around 1000 to 1400 cm\(^{-1}\). According to Figure 3.2(c), the biodiesel samples showed more unsaturated bonds in the range of 1700 to 1800 cm\(^{-1}\) than saturated ULSD. Those molecules in the double bond region are generally considered oleic (C18:1), linoleic (C18:2), and linolenic (C18:3) acids (Issariyakul and Dalai, 2014). SME contains a FAME which is observed at 1742 cm\(^{-1}\) in the FTIR spectrum by a strong carbonyl (C=O) signal (Zhang, 2012). This unsaturated carbonyl signal is also depicted for TO and WCO and compared with SME in Figure 3.2(c). The absorbance peak for SME at 1742 cm\(^{-1}\) in Figure 3.2(c) was 0.37% which is slightly higher than the peaks for TO and WCO (both 0.34%). More double
bonds (unsaturation) as mentioned earlier represent a high IV, which exhibits more NOx emissions (Sarathy et al., 2007; Benjumea et al., 2011). These double bonds are prone to oxidation through the radical chain reaction (Bouaid et al., 2007; Jain and Sharma, 2011). Figure 3.2(d) shows that the amount of C-H bonds in ULSD fuel is higher than biodiesel fuels. ULSD has more carbon content than any other biodiesel fuels and it releases more energy during the combustion (Agarwal and Das, 2001; Demirbas, 2007).

Figure 3.2(a–d) shows that the spectrum of TO is qualitatively similar to that of WCO. SME, TO and WCO showed significant differences from ULSD in the number of double bonds (unsaturated chains) as shown in Figure 3.2(c). A comparison of the biodiesel fuels with the one obtained from other feedstocks indicates that it is difficult to identify any significant difference in the degree of unsaturation within the WCO and TO fuels based on the FTIR results although SME showed a relatively high degree of unsaturation in the chemical structure as presented in Table 3.1.
3.3.2 Experimental Setup

Combustion tests are carried out in a laboratory reactor (300 ml) purchased from Parr Instrument Company. The device included a stainless steel reactor (2.5” inside diameter with 4.0” inside depth) placed in an electrically heated chamber. A J type thermocouple was placed inside the reactor for temperature recording, and a temperature controller was installed to preserve the reaction conditions at the predetermined values. With this arrangement, the reaction temperature could be controlled and monitored with a precision of 0.1°C. A compressed air tank was used to maintain the combustion condition. A schematic diagram of the entire experimental setup is shown in Figure 3.3.
3.3.3 Experimental Procedure

Experiments are conducted in a combustion chamber as a single cycle of combustion in an engine cylinder. The amounts of fuel and air are determined to keep the air-fuel ratio as one. To estimate the air-fuel ratio, \( \Phi \), stoichiometric conditions will be calculated from a mixture of various esters as a representative for a biodiesel fuel as shown in Table 3.1. Stoichiometric combustion occurs when all the oxygen is consumed in the reaction, and there is no molecular oxygen in the products.

Fuel was placed inside the reactor at room temperature and air is injected from a high pressure air tank (dried air purchased from Airgas®) into the chamber while the pressure is being monitored. The combustion process can be called as premixed combustion because the oxygen came into contact with the fuel before combustion. Then the heater is turned on to elevate the temperature until the fuel ignited. The ignition point of combustion is determined by observing the combustion peak for temperature and pressure via a computer software program and pressure gauge provided by Parr Instrument. The elapsed time to observe ignition temperature peak is named as ignition delay and the value of temperature is named as ignition temperature as shown in Figure

Figure 3.3. Schematic diagram of experimental set-up.
3.4. After ignition terminated, the combustion gases are released and allowed to pass through a PTFE membrane filter capsule with 0.2 μm pore size that is placed before the NOx analyzer. NOx data are recorded as the gases passed through the detector until the reactor depressurized. A Shimadzu 2010 (Shimadzu, Kyoto, Japan) GC, equipped with a pulsed discharge helium ionization detector (PDHID) was used for exhaust analysis. The type of column used for GC was Carboxene 1010 PLOT (Sigma-Aldrich, USA), 30 m in length and 0.53 mm in diameter. After combustion, soot samples are collected from combustion chamber for further analysis. All the instruments (listed below) will be calibrated with standard protocols provided by the manufacturers prior to the tests.

![Graph](image.png)

Figure 3.4. Example of defined ignition delay and ignition temperature measurement.

### 3.3.3.1 FTIR Analysis of the Samples

FTIR (UMA-600 Microscope, Varian Excalibur Series, Digilab) analysis is conducted on the biodiesel samples with the maximum scan rate with the resolution of 1 cm\(^{-1}\) between 650 to 4000 cm\(^{-1}\) as shown in Figure 3.5. For the soot samples collected from the combustion chamber, FTIR spectroscopy is carried out using a PerkinElmer
Frontier™ FTIR spectrophotometer (Figure 3.6) equipped with a Spectrum 10.4.2™ software suite within the range of 800 to 4000 cm\(^{-1}\). Samples will be prepared in the form of pressed wafers (1% sample in potassium bromide or KBr) for analysis.

![Figure 3.5. FTIR instrument used in this study to analyze liquid biodiesel fuels and soot particles.](image)

![Figure 3.6. FTIR instrument used in this study to analyze soot particles](image)

### 3.3.3.2 TEM Analysis of Soot Particles

The information on the size and morphology of soot is obtained using TEM (Figure 3.7). First, a small amount of soot approximately 0.1 mg will be transferred to a separate centrifuge tube and well mixed with about 5 ml of isopropanol. Then, a drop of five minutes sonicated suspension will be deposited on PELCO® TEM grid support films of carbon (300 mesh Au) and placed in a Hitachi HD-2300A (Hitachi, Japan) microscope
operated at a voltage of 200 kV. Measurement of the particle size of soot in collected images will be done using a software program, Quartz PCI (version 8), at 110 K magnification.

Figure 3.7. TEM instrument used in this study to analyze soot particles

### 3.3.3.3 Elemental Analysis of Soot Particles

ICP-MS is a highly sensitive and accurate method for quantifying the elemental composition of soot particles. ICP-MS analyses are performed on a quadrupole instrument as shown in Figure 3.8 (XSeries II, Thermo Fisher Scientific, Inc., Bremen, Germany). The data obtained from ICP-MS represent bulk analysis and not the surface analysis that can be done with energy dispersive X-ray (EDX) spectroscopy. Because of low-sulfur content, high ionization potential and low sensitivity of the instrument on sulfur content, the concentration of sulfur included in ULSD may not be detected by ICP-MS.
3.3.3.4 TGA Analysis of Soot Particles

TGA analysis of the collected soot is carried out using a Q50 TGA (TA Instruments, USA) under nitrogen and oxygen atmosphere as shown in Figure 3.9. The soot is placed in a platinum pan and then temperature is ramped first from room temperature up to about 400 °C under nitrogen environment and then to about 750 °C under oxygen environment at a heating rate of 5 °C/min. A balance purge flow of 40 mL/min and sample purge flow of 60 mL/min are used for analysis. It is expected that at this high temperature all the dry carbon materials present in soot would be oxidized. TGA is calibrated with the predefined standard operating procedures and tuning solutions prior to any tests.
3.3.3.5 NOx Analyzer

NOx emissions will be measured by using a NOx gas analyzer (MEXA-720, Horiba) as shown in Figure 3.10. It is a direct-installation gas analyzer using a zirconia ceramic sensor whose response time is about 0.7 second. Standard laboratory instruments and procedures provided by the company are used to calibrate NOx analyzer. The main specifications of the NOx gas analyzer are given in Table 3.2.
Figure 3.10. NOx analyzer instrument used in this study to analyze NOx emissions.

Table 3.2. Specification of Horiba NOx analyzer

<table>
<thead>
<tr>
<th>Component</th>
<th>NOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ranges</td>
<td>0-3K ppm</td>
</tr>
<tr>
<td>Accuracy</td>
<td>0-1000 ppm: ±30 ppm with 3 point calibration</td>
</tr>
<tr>
<td></td>
<td>1001-2K ppm: ±3% of reading with 3 point calibration</td>
</tr>
<tr>
<td>Warm-up time</td>
<td>Approximately three minutes after turned on.</td>
</tr>
<tr>
<td>Sample gas conditions</td>
<td>Stoichiometric to lean for diesel or lean-burn engines.</td>
</tr>
<tr>
<td></td>
<td>Measurement gas temperature: -7 to 800°C</td>
</tr>
<tr>
<td>Ambient conditions</td>
<td>For main unit: 5 to 45°C; (operating), -10 to 70°C (storage)</td>
</tr>
<tr>
<td></td>
<td>Less than 80% relative humidity</td>
</tr>
</tbody>
</table>

3.4 Results and Discussion

3.4.1 Ignition Delay and Temperature

The ignition temperature and ignition delay were defined to determine how these combustion parameters are related to fuel's unsaturation degree (Figure 3.4). The average values of ignition delay and ignition temperature along with their standard deviations are depicted in Figure 3.11(a,b), respectively. Unsaturated structures and relatively long chain fatty acids in biodiesel fuels are reported to non-linearly slow down the combustion compared to saturated fuel such as ULSD. SME has a higher percentage of unsaturation, and therefore, it has a longer ignition delay as compared to TO and WCO.
Figure 3.11(b) shows that ULSD released higher energy at the ignition point than the other biodiesel samples, which indicates its higher heating value compared with biodiesel fuels (Agarwal and Das, 2001; Knothe, 2005; Demirbas, 2007). The higher the ignition temperature was, the shorter the ignition delay (Basha et al., 2009; Caresana, 2011). As shown in Figure 3.11(b), the ignition temperature of ULSD reached 415.6 ± 1.4°C, while for the biodiesel combustion, the average ignition temperature barely reached 355.1 ± 5.2, 346.1 ± 6.6, and 331.8 ± 6.7°C for SME, TO, and WCO, respectively. As the content of biodiesel increased in the blends, the ignition temperatures decreased. In other words, as the oxygen content of the fuels increased in the blends, the ignition temperature decreased due to their low-carbon content and low heating values (less C-H and C-C bonds than ULSD) of methyl esters (Knothe, 2005). In general, the values of combustion heat of biodiesel fuels are within the range of 75.6–89.9% that of regular diesel (Ng et al., 2010).
Figure 3.11 (a) Ignition delays and (b) ignition temperatures of different biodiesel fuels (SME, TO, and WCO, respectively) blended with ULSD. Error bars represent standard deviations.

As mentioned earlier, properties of different types of biodiesel have a strong relation with their fatty acid composition. The results in Figure 3.11(a,b) indicate that ignition delay and ignition temperature of biodiesel fuels are related to the unsaturation of the alkyl chain, especially of the number of double bonds (C18:1 to C18:3) in the fuel. In other words, SME had the highest amount of double bonds (highly unsaturated with C18:2 and C18:3) compared with the other fuels, while it had the highest ignition delay.
The fully saturated fuel (ULSD with ignition temperature of 415.6 ± 1.4°C) showed the lowest ignition delay and highest ignition temperature. Ignition temperature of ULSD was about 2 min earlier than any of the other fuels.

3.4.2 NOx Emissions

NOx formation mechanisms are complex and are caused by a number of coupled mechanisms, whose effects may tend to reinforce or cancel one another under different combustion conditions of an engine as well as fuel characteristics (Mueller et al., 2009). So far, it can be concluded that combustion temperature and the degree of unsaturation are two major parameters that play important roles on NOx emissions in the laboratory combustion chamber. In addition, NOx emissions from biodiesel combustion may be associated with the oxygen content of FAMEs because the fuel oxygen may provide additional oxygen for NOx formation.

Figure 3.12 represents the average values of five data sets which are plotted with standard deviations. In the case of ULSD combustion, due to the presence of more C-C and C-H bonds (e.g., a higher carbon content which means a higher heating value) than biodiesel fuels (Demirbas, 2007), high combustion temperature might be a more influential parameter on NOx formation than it is in biodiesel combustion (Plee et al., 1982).
Figure 3.12. Variation of NOx emissions with respect to their degrees of unsaturation at LTC. Error bars represent standard deviations.

As shown in Figure 3.12, it can be observed that NOx emissions varied in terms of the degree of unsaturation of the fuel when biodiesel fuels were included in the samples. In agreement with other published results, it is observed that NOx emissions increased by increasing the number of double bonds of FAMEs (McCormick et al., 2001; Graboski et al., 2003; Bao and He, 2006; Szybist et al., 2007; Lapuerta et al., 2009; Benjumea et al., 2011; Bunce et al., 2011). In other words, NOx emissions decrease with a high degree of saturation of FAME chain. The results shown in Figure 3.12 confirmed that the condition for NOx formation would be the presence of oleic fatty acids (C18:1 to C18:3). This conclusion is readily represented in the NOx results of SME, TO, and WCO. TO and WCO showed less NOx than SME which has the highest amount of double bonds (C18:2 and C18:3), where the major portion of double bonds in TO and WCO were found in C18:1 molecules as shown in Table 3.1. NOx emissions were reduced with a large portion of oleic fatty acids, C18:1, and increased with a portion of linoleic fatty acids,
C18:2, in biodiesel fuels. Zhang and Boehman (2007) argued that the presence of double bonds in biodiesel leads to the formation of free radicals that advances NOx formation. The average reduction of NOx was calculated 3–5% less for all the tested biodiesel samples than ULSD under LTC conditions. The observed variation of standard deviations in the combustion and emission results could be due to the variation in the fuel's composition in each run. Thus, biodiesel fuels, those with less double bonds in fatty acid chains, appear to have the lowest NOx emissions.

3.4.3 Paired T-Test Analysis on NOx Emissions

A statistical analysis of the data (paired t-test) was used to assess the statistical significance of the differences between the NOx emissions for the fuel blends. The difference in NOx emissions among ULSD and all the biodiesel samples were compared statistically based on the paired t-test comparison of the means and assuming the equal variance with a p-value <0.001 and 95% confidence for all comparisons. For the paired t-test, it was hypothesized that there was a highly significant difference in the NOx emissions between two selected samples from different feedstocks where the p-value ≤0.001. In addition, it was considered statistically significant when the p-value ≤0.05 approximately. It is worth to mention that p-value and t-value are dimensionless parameters.

Using the simple paired t-test analysis for all the samples, the results indicated that the differences between the samples are not considered statistically significant in most cases (presented in white color) as shown in Table 3.3. On the other hand, the cases of which the differences appear to be highly significant and significant are presented in black and gray color, respectively.
The t-test results are summarized in Table 3.3. No statistically significant differences in the NOx concentrations were observed among neat biodiesel fuels while ULSD had significant difference with neat TO and WCO, and marginally significant difference with neat SME. Potential significance of the NOx emission differences between a pair of SMEB20 and TOB100 and a pair of WCOB20 and WCOB100 were considered significant and are shown in the black boxes. Also, SMEB20 had a significant difference when compared with TO and WCO in neat form and even in WCOB50. For the results in the black boxes with 95% confidence, the null hypothesis can be rejected. The t-test results suggest that the feedstock type could possibly have a significant effect on NOx emissions.

There are also some cases labeled in gray color that represent significant effects on NOx reduction with 95% of confidence levels. The results indicate that TO and WCO reduced NOx formation significantly as compared to ULSD and SME in many blends.

Table 3.3. Results of paired t-test analysis on fuels tested for NOx emissions.

<table>
<thead>
<tr>
<th></th>
<th>SMEB20</th>
<th>SMEB50</th>
<th>SMEB100</th>
<th>TOB20</th>
<th>TOB50</th>
<th>TOB100</th>
<th>WCOB20</th>
<th>WCOBS0</th>
<th>WCOB100</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULSD</td>
<td>P = 0.15</td>
<td>t = 1.45</td>
<td>P = 0.04</td>
<td>t = 2.07</td>
<td>P = 0.30</td>
<td>t = 1.04</td>
<td>P = 0.05</td>
<td>t = 1.96</td>
<td>P &lt; 0.0001</td>
</tr>
<tr>
<td>SMEB20</td>
<td>P = 0.61</td>
<td>t = 0.52</td>
<td>P = 0.15</td>
<td>t = 1.43</td>
<td>P = 0.80</td>
<td>t = 0.26</td>
<td>P = 0.21</td>
<td>t = 1.25</td>
<td>P &lt; 0.0001</td>
</tr>
<tr>
<td>SMEB50</td>
<td>P = 0.32</td>
<td>t = 1.00</td>
<td>P = 0.93</td>
<td>t = 0.09</td>
<td>P = 0.44</td>
<td>t = 0.78</td>
<td>P = 0.02</td>
<td>t = 2.36</td>
<td>P = 0.83</td>
</tr>
<tr>
<td>SMEB100</td>
<td>P = 0.35</td>
<td>t = 0.94</td>
<td>P = 0.80</td>
<td>t = 0.26</td>
<td>P = 0.72</td>
<td>t = 1.52</td>
<td>P = 0.83</td>
<td>t = 0.26</td>
<td>P = 0.39</td>
</tr>
<tr>
<td>TOB20</td>
<td>P = 0.47</td>
<td>t = 0.73</td>
<td>P = 0.08</td>
<td>t = 1.75</td>
<td>P = 0.80</td>
<td>t = 0.25</td>
<td>P = 0.23</td>
<td>t = 1.20</td>
<td>P = 0.07</td>
</tr>
<tr>
<td>TOB50</td>
<td>P = 0.43</td>
<td>t = 0.79</td>
<td>P = 0.53</td>
<td>t = 0.63</td>
<td>P = 0.84</td>
<td>t = 0.20</td>
<td>P = 0.37</td>
<td>t = 0.90</td>
<td>P = 0.07</td>
</tr>
<tr>
<td>TOB100</td>
<td>P = 0.03</td>
<td>t = 2.19</td>
<td>P = 0.03</td>
<td>t = 2.19</td>
<td>P = 0.13</td>
<td>t = 1.52</td>
<td>P = 0.81</td>
<td>t = 0.24</td>
<td>P = 0.08</td>
</tr>
</tbody>
</table>
3.4.4 TEM Analysis of Soot Particles

A significant reduction in the mass of soot particles was observed in the biodiesel combustion for all of the biodiesel samples compared with the ULSD result. For pure biodiesel samples (B100), no soot particle was observed inside of the combustion chamber. The size of soot particles from laboratory study was determined using TEM images as shown in Figure 3.13. From the ten images taken for each sample, one hundred soot particles were measured precisely to obtain the average size distributions of soot particles. TEM study demonstrated that soot particles were almost spherical in shape and aggregated to form agglomerate structures. As shown in Figure 3.13, the clusters of particles per unit area involve the continuous bonding of particles to form a large network of carbon soot particles.

The average diameters of the soot particles and their standard deviations (STD) are listed in Table 3.4. STD shows deviation of soot particle diameters from mean values. As shown in Table 3.4, soot particles from the ULSD sample had the greatest diameter (95.2 nm) than other biodiesel blends. For biodiesel samples, the soot particles from B20 samples were slightly larger than B50 soot particles. The soot particle diameters of SMEB20 and 50 are greater than those of TOB and WCO, respectively.
Both TOB and WCO show not much difference in soot particle diameter for the corresponding blends. The results confirmed previous findings where Lapuerta et al. (2008) concluded that unsaturated biodiesel fuels showed a smaller mean particle diameter than less unsaturated fuels. Moreover, as the fuel became more unsaturated, soot emissions decreased. These results indicate the relations of the amount of biodiesel included in the blends and the degree of unsaturation with the soot particle size.

In addition to the low numbers of species that undergo soot inception and mass growth in biodiesel fuels (Kumar et al., 2014; Omidvarborna et al., 2015b), it is speculated that the number and amount of soot particles decreased because soot particles were further oxidized due to the oxygenated fatty acids in biodiesel (Kohse-Höinghaus et al., 2010). It is also reported that unsaturated FAMEs led to the generation of higher levels of oxygenated species (Sarathy et al., 2007). The results were in agreement with Ishiguro et al. (1991) and Harris and Maricq (2001), where they concluded that the further oxidation process arising from biodiesel may shift the typical size distributions of diesel soot particles.
Table 3.4. Details on soot particle size distribution from different biodiesel feedstocks and blends with ULSD

<table>
<thead>
<tr>
<th>Fuel</th>
<th>ULSD</th>
<th>SMEB20</th>
<th>SMEB50</th>
<th>TOB20</th>
<th>TOB50</th>
<th>WCOB20</th>
<th>WCOB50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average (nm)</td>
<td>95.2</td>
<td>88.3</td>
<td>87.9</td>
<td>93.7</td>
<td>92.5</td>
<td>91.8</td>
<td>90.1</td>
</tr>
<tr>
<td>STD</td>
<td>35.9</td>
<td>26.3</td>
<td>24.0</td>
<td>21.9</td>
<td>21.4</td>
<td>24.5</td>
<td>22.7</td>
</tr>
</tbody>
</table>

Unlike the ULSD soot particles, it was observed that the samples of SME, TO, WCO blends produced normal distributions in the range of 50 to 150 nm. As shown in Figure 3.14, soot particles larger than 175 nm were formed only in the combustion of ULSD. The size distribution of ULSD did not follow the same trend as other biodiesel fuels where they exhibited a quasi-monodispersed structure (Smekens et al., 2005). The large diameter of the ULSD soot particles can be partially attributed to the combustion conditions that took place in the combustion chamber. Due to the higher heating value of ULSD than biodiesel (Omidvarborna et al., 2015c), ULSD generates higher temperature and pressure that facilitate the growth of soot particles. Consequently, formation of soot particles is initiated by the inception of precursors such as acetylene and PAHs, and the high temperature and pressure of combustion enhance the growth of soot particles in diesel combustion. It turns out that the addition of biodiesel in blends reduces the inception of soot precursors, and in addition it reduces the size and number of soot particles through further oxidation with extra oxygen included in biodiesel (Lapuerta et al., 2007; Omidvarborna et al., 2015c). This result was in agreement with Lapuerta et al. (2008), where they reported that an increase in the proportion of biodiesel in blends resulted in a decrease in mean particle diameter of soot particles.
3.4.5 Structure of Oxidized Soot Particles in Biodiesel Combustion

In the combustion of biodiesel fuel, biodiesel's extra oxygen molecules are involved in the various side reactions, which may eliminate soot inceptors and soot growth species (Omidvarborna et al., 2015b). Generally after formation, soot particles initially possess the typical shell–core structure (Hurt et al., 2000). Biodiesel soot particles, produced especially from high percentage biodiesel blends, are reported to exhibit fast and capsule-type oxidation to become hollow inside (Song et al., 2006). During oxidation, a uniform structure of soot particles is deformed from inside to become a non-uniform structure as explained by Song et al. (2006). The depletion of inner material leads to more disordered arrangement in the structure of outer shell (Song et al., 2006). Thus, biodiesel soot particles experienced structural changes as shown in Figure 3.15. The arrows in Figures 3.15(a–c) indicate possibly an example of oxidation deformation in the structures of soot particles from the combustion of all biodiesel blends.
More details are presented to support the oxidation of soot particles in Figure 3.15(d–f) which are the magnified images of oxidized soot particles at 100 k, 200 k, and 400 k magnifications. TEM images taken at low magnification show a different morphology for oxidized soot particles compared to normal soot particles. Any specific difference is not observed among oxidized soot particles based on their saturation degrees. The results can confirm Hurt et al. (1993) explanation where they emphasized the importance of inner structural changes during the oxidation process.

A diameter change was experimentally observed in oxidized soot particles and as Hurt et al. (1993) claimed that the internal oxidation rate is greater than the surface oxidation rate. The results confirmed that soot particle diameters decreased during oxidation process.

![Figure 3.15](image)

Figure 3.15. Sample soot particle oxidation in the formation process for the different feedstock biodiesels. (a-c) Observed deformation in the structure of soot particles by the oxidation process for SME, TO, and WCO, respectively, (d-f) Images of oxidized soot particles magnified by 100k, 200k, and 400k, respectively. Arrows indicate enlargement of the selected area that are presented in the next images for better comparison.
3.4.6 Elemental Analysis of Collected Soot Particles

The source of many elements may originate from organic and inorganic components, metals, or complexes present in various feedstocks. Some of these elements can be converted into aerosols during the combustion processes. Alkali (Na) and alkaline earth (Ca) elements may possibly come from the transesterification process in biodiesel production.

Figure 3.16 summarizes the results of elemental analysis of the soot particles obtained from the blend of various feedstocks. Eight major elements were identified in the elemental analysis of soot particles: aluminum (Al), calcium (Ca), copper (Cu), iron (Fe), magnesium (Mg), molybdenum (Mo), sodium (Na), and potassium (P). Compared with the existing data collected from field tests that include elements originated from engine parts and oils (Omidvarborna et al., 2014; Shandilya and Kumar, 2014; Kumar et al., 2014), these eight elements detected in this study came from the tested fuel itself and represented the type and amount of different elements produced under the tested conditions. Some authors have reported that elements such as Zn and Cr may be produced from the unwanted combustion of lubricants and their additives (Shandilya and Kumar, 2014). These elements were not detected here because of the absence of lubricants in the laboratory combustion chamber. In addition, in this test series combustion happened at low-temperature. Literature study proved that higher temperature intensifies the portion and number of emitted elements in engine exhaust (Salamanca et al., 2012b; Omidvarborna et al., 2014).

Sulfur that appears in the soot particles normally comes from regular diesel. The sulfur content is not reported in elemental analysis due to low sulfur content of ULSD and low sensitivity of ICP-MS instrument (sulfur has shown high ionization potential).
As shown in Figure 3.16, the ratios between detected elements do not show significant difference. Thus, the types of biodiesel feedstocks do not seem to be a source of differences in the number and amount of detected elements under the low-temperature condition. It appears that Na, Mg, Ca, Fe, Mo, and Cu, Al, and P at very low percentages are the marker metals of both ULSD and biodiesel blends (from SME, TO, WCO feedstocks) under LTC.
Figure 3.16. Elemental analysis of the collected soot particles from different feedstocks and blends with ULSD, (a) ULSD, (b-1) SMEB20, (b-2) SMEB50, (c-1) TOB20, (c-2) TOB50, (d-1) WCOB20, and (d-2) WCOB50.

3.4.7 FTIR Spectra of Collected Soot Particles

The molecular structures of soot particles were characterized using FTIR analysis. The FTIR spectra of collected soot particles from the combustion of ULSD and three different B20 biodiesel fuels are presented in Figure 3.17. In the diesel soot spectra, the most characteristic signals are sulfur bonds (Salamanca et al., 2012a). The sulfur bonds reported by Cain et al. (2010) were detected around 1000 and 1100 cm\(^{-1}\) (Figure 3.17(a)).
This is in agreement with results reported in the literatures, where the emissions of sulfur by a series of biodiesel fuels or their blends are significantly smaller, which in turn favors the reduction of soot particles, since the nucleation process by the sulfur mechanism is reduced (Vander Wal et al., 2010; Salamanca et al., 2012b). The origin of this signal is attributed to the sulfur present in the ULSD, although sulfur is not detected in liquid fuel by using FTIR. Thus, it can be inferred that sulfur-derived species were adsorbed on soot particles after combustion.

Other small peaks in the range of 1350–1370 cm\(^{-1}\) and 1475–1550 cm\(^{-1}\) are related to alkanes (C–H) and nitro compounds (N–H), respectively. In Figure 3.17(a), the small aromatic peaks are observed at around 1500 cm\(^{-1}\) (C–C aromatics in-ring) and around 1610 cm\(^{-1}\) for stretching aromatics. The larger is the aromatic related signal, the less the hydrogen content becomes.

The presence of aliphatic groups (C–H) helps to maintain the interconnection of PAHs within the network (Santamaria et al., 2010). Aliphatic groups are reported to increase the mass of soot particles during the mass growth step (step 3) in early stages (Kumar et al., 2014; Omidvarborna et al., 2015b). The presence of aliphatic spectra may come from unburned HCs condensed on the surface of soot particles at low-temperature (Schönborn et al., 2009; Vander Wal et al., 2010). As shown in Figure 3.17(a), carbonyl content (esters, alpha and beta-unsaturated esters, etc. at around 1665 to 1760 cm\(^{-1}\)) of the soot samples were negligible compared to the original peaks of the biodiesel blends in Figure 3.2. It means that carbonyl bonds (C=O) in biodiesel blends disappeared during the combustion as they provide extra oxygen for combustion.
The prominent broad and intense peak between 3100 cm\(^{-1}\) and 3640 cm\(^{-1}\) observed in the spectrum of Figure 3.17(b) is a contribution from a variety of –OH stretching modes. OH spectrum may be a signature of the absorption of many different chemical compounds which include alcoholic groups. The OH spectrum of SME may be related to its unsaturation degree. As the biodiesel fuels become more unsaturated, the oxygen content may increase. This is because of the decrease in the molecular weight associated with the displacement of two hydrogen atoms by a double bond (Benjumea et al., 2011).

Although the signal strength of biodiesel fuels was significant and comparable with that of ULSD for some regions (e.g., 1000–1100 cm\(^{-1}\) and 3100–3640 cm\(^{-1}\)), soot particles obtained from the biodiesel samples showed relatively lower sulfur and higher oxygen content than the ULSD soot sample. The sulfur content in ULSD was reported to enhance the nucleation of soot particles and results in the large mass of soot (Vander Wal et al., 2010). Therefore, the low sulfur content of biodiesel may be attributed to the soot particles size reduction.
Figure 3.17. Infrared spectra of soot particles produced from ULSD and blended biodiesel samples from different feedstocks such as SMEB20, TOB20, and WCOB20, (a) from 800 to 1800 cm\(^{-1}\) and (b) from 2800 to 3800 cm\(^{-1}\).

3.4.8 TGA Analysis of Collected Soot Particles

Literature study showed that the morphology and reactivity of the soot particles emitted from a diesel engine were more affected by the fuel composition (diesel and
animal fat biodiesel) than by the engine operation mode (Lapuerta et al., 2012). Therefore, a set of TGA experiments was performed to investigate the amount of volatile organic fraction (VOF) and carbon fraction of diesel soot particles to determine the oxidation behavior of soot particles. Table 3.5 and Figure 3.18 show the result of TGA analysis of collected soot particles of ULSD and B20 of all biodiesel fuels from the combustion chamber.

In the presence of nitrogen, a slow 5 °C/min ramp was employed to volatilize the vast majority of the organic compounds until 400°C. Before switching to the oxygen environment at 400°C, usually thermal decomposition happens with the formation of gaseous reaction products, where the amount of moisture and VOF were determined. After 400°C, when the media changed from nitrogen to oxygen, it is assumed that unburned carbon was oxidized. The oxidation rate of biodiesel fuels is faster than that of ULSD and it occurs earlier than ULSD as shown Figure 3.18(a). As shown in FTIR analysis (Figure 3.17), soot particles produced in biodiesel combustion may be more readily oxidized than soot particles from ULSD combustion. This phenomenon, observed previously in Section 3.4.5 (Figure 3.15), accelerates oxidation of soot particles collected after combustion of biodiesel fuels. Table 3.5 shows a proximate analysis of collected soot particles determined by TGA result.

Table 3.5. Proximate analysis of collected soot particles from B20 biodiesel fuels and ULSD and their peak temperatures by TGA analysis.

<table>
<thead>
<tr>
<th>Fuel type</th>
<th>Weight loss (%) by 400°C</th>
<th>Weight loss (%) after 400°C</th>
<th>First peak temperature (°C)</th>
<th>Second peak temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULSD</td>
<td>5.86</td>
<td>94.14</td>
<td>---</td>
<td>624.00</td>
</tr>
<tr>
<td>SMEB20</td>
<td>3.91</td>
<td>96.09</td>
<td>517.21</td>
<td>602.97</td>
</tr>
<tr>
<td>TOB20</td>
<td>5.82</td>
<td>94.18</td>
<td>512.82</td>
<td>600.47</td>
</tr>
<tr>
<td>WCOB20</td>
<td>5.48</td>
<td>94.52</td>
<td>505.31</td>
<td>609.86</td>
</tr>
</tbody>
</table>
The increase of the heater temperature made soot particles to further oxidized, and the derivative weight loss curve in Figure 3.18(b) identifies the point at which the weight loss due to soot particle oxidation is most evident. ULSD has only one peak and have the length of the peak longer than that of biodiesel blends because ULSD has the greater carbon content than that of biodiesel fuels. Biodiesel blends showed two peaks, the first one obtained from HC oxidation and the second from carbon oxidation (Laosuwan et al., 2011). The values of the ignition peaks are observed at lower temperature for biodiesel blends due to their chemical structure. According to Boehman et al. (2005), due to the oxygenated structure and various unsaturation levels, biodiesel had a lower oxidation temperature compared with diesel, while amorphous carbon was found in the inner core of soot particles. The hollow internal structure of biodiesel soot particles, likely created by the fuel-bonded oxygen, enables a much higher oxidation rate compared with the soot particles generated by diesel (Song et al., 2006). As a result this leads to a more amorphous soot particle structure which in turn enhances the rate of soot particle oxidation. Thus, there are inherent differences in the reactivity of the soot particles between ULSD and biodiesel fuels.
Figure 3.18. TGA curves (weight loss (a) and derivative weight (b)) for soot particles taken directly from the combustion chamber (mass of soot particles was around 3 mg).
3.4.9 Carbon Emissions (CO, CO₂, and CH₄)

For biodiesel fuels, the changes in the carbon emissions vary according to the type of chemical characteristics of the feedstocks. Figures 4.19(a-c) represent the exhaust emissions of CO, CO₂, and CH₄ in relation to the biodiesel percentages, respectively.

As the local temperature is not high enough at the early stage of combustion, very little oxidation reactions take place. At this stage, primary reactions can take place and the initial HCs may be produced. In ULSD combustion, the uneven distribution and lack of oxygenated molecules across the combustion chamber may cause local oxygen deficiency and incomplete combustion, which results in more CO formation. A drastic reduction on CO exhaust emissions was observed when biodiesel blends were used instead of ULSD. The results confirmed that ULSD emits higher CO (2.5 mole %) and lower CO₂ (0.7 mole %) than the other blends. For the biodiesel fuels in Figure 3.19(a), biodiesels’ higher oxygen-to-carbon ratios compared to ULSD are thought to be the main reason for the significant decrease in CO emissions. Moreover, the presence of peroxides and hydro-peroxides formed during biodiesel combustion might have resulted in the lower emissions of CO in biodiesel than that of ULSD (Monyem and Van Gerpen, 2001). On average, the highest reduction rate for CO was observed in the TOB100 emissions compared to ULSD by around 79%. The reductions of CO emission for pure WCO and SME were 64% and 60% less than ULSD’s CO emissions, respectively.

For the biodiesel fuels, the reduced CO emissions can be explained by the higher oxygen content in the short fatty acid molecules of TO (C16:0 or less), which leads to a more complete combustion as pointed out earlier (Pinzi et al., 2013). Short chain length of FAMEs makes it easier to oxidize than the long chain FAMEs, and therefore, a further reduction of CO emissions can be achieved using biodiesel fuels containing an increased
content of short FAME chains. Moreover, FAMEs with longer chain length and unsaturated structure (e.g. SME) have higher boiling and melting points (Pinzi et al., 2013) than shorter chain FAMEs (e.g. TO and then WCO), so they are less likely to be completely vaporized and burnt, thereby increasing CO emissions (Hansen and Jensen, 1997).

Besides, CO emissions are reported to increase with increasing the number of double bonds in the chain lengths of FAMEs (Pinzi et al., 2013). For biodiesel fuels used in this study, the carbon content increases with an increase in the unsaturated contents and chain lengths (especially for C18:0 to C18:3), which means SME possibly emits more CO than WCO and TO, respectively. The obtained emission result in Figure 3.19(a) is in agreement with the EPA’s survey, where the reduction of CO emission from pure biodiesel was reported 47% on average of the CO emission from ULSD (EPA, 2002).

In contrast with CO emission reduction, CO₂ emissions in the exhaust increase with decreased chain length of FAMEs as shown in Figure 3.19(b). Higher CO₂ emissions were reported with decreased chain length of pure FAMEs (Pinzi et al., 2013). This trend can be explained by the higher oxygen content in the shortest fatty acid molecules as well as relatively lower content of carbon in biodiesel than ULSD for the same volume of the fuel consumed, which lead to emit more CO₂ emissions (Rakopoulos et al., 2004; Lapuerta et al., 2008; Chauhan et al., 2012). As noted earlier, shorter molecular structure of FAMEs helps faster fuel evaporation which results in possibly more complete combustion. For SME, the CO₂ formation increased by a factor of 2.9, while the CO₂ increased by a factor of 3.0 and 3.2 on average for WCO and TO from ULSD, respectively.
CH₄ emissions increased as the portion of biodiesel increased in the blends as shown in Figure 3.19(c). Although CH₄ may be regarded as an intermediate species in biodiesel combustion, clear trends of CH₄ emissions were observed when the unsaturation level of methyl esters was varied. In accordance with Hansen and Jensen (1997), CH₄ emissions considerably increased with an increasing number of double bonds. Short and less unsaturated FAMEs such as WCO and TO showed lower emissions of CH₄ than unsaturated and longer chain FAMEs such as SME. Although FAMEs take highly complex reaction paths with respect to ULSD, it may be possible to improve CH₄ emissions from biodiesel combustion by increasing the contents of short and saturated FAMEs. The results showed that the average CH₄ formation was increased by a factor of 1.9 for pure biodiesel fuels with respect to ULSD. For pure biodiesel fuels, SME produce the highest CH₄ at 2.7 mol%, WCO at 2.4 mol%, and the TO at 2.3 mol%.
Figure 3.19. Primary combustion gases in mole percent emitted during the combustion of fuels (a) CO emissions, (b) CO$_2$ emissions, (c) CH$_4$ emissions. B0 represents ULSD combustion emissions.

3.5 Conclusion

3.5.1 NOx Emissions
A range of biodiesels of varying degrees of unsaturation were tested for their NOx emissions using a laboratory combustion chamber and compared to ULSD. From the
experiments carried out to investigate the effects of the type of feedstock on ignition temperature, ignition delay, and NOx emissions, the following conclusions can be drawn:

1. FTIR was used to qualitatively determine the content of FAME in biodiesel fuels. FTIR analysis of biodiesel fuels proved that there was no distinction among the selected biodiesel fuels under FTIR study. Functional groups were observed at relatively the same absorbance.

2. Under LTC conditions, the ignition delay time increased and ignition temperature decreased when the percentage of biodiesel in the blends increased. The ignition temperatures of neat biodiesel samples decreased relatively in the order of SME (the highest), TO, and WCO (the lowest).

3. The difference in NOx emissions between the neat biodiesel samples and ULSD was determined for selected fuels. The degree of unsaturation of biodiesel appeared to have a proportional relationship with NOx emissions. When the average values were compared, SME produced more NOx emissions than TO and WCO. Highly unsaturated molecules in biodiesel such as C18:2 and C18:3 appeared to cause more NOx emissions. Biodiesel with saturated chains would help reduce NOx emissions. It can be concluded that double bonds in FAMEs (C18:2 and C18:3) had a significant impact on the formation of NOx, while oleic fatty acid (C18:1) helped NOx formation reduce.

4. The paired t-test results indicated that there were significant differences in NOx emissions between the neat biodiesel samples (e.g., TO100, WCO50, and WCO100) and ULSD. Additionally, there were pairs that may cause relatively significant differences in NOx reduction.
3.5.2 Soot Emissions

In this study, collected soot particles during combustion of ULSD and various biodiesel feedstocks were characterized with different techniques. The results confirmed that emissions of soot particles from biodiesel fuels are significantly less than ULSD. This reduction became even greater with the increase of biodiesel proportion in the blended fuels. The reduction of soot particles from the combustion of biodiesel fuels is mainly due to the oxygen content and unsaturation degree of FAMEs as well as lack of aromatic and sulfur compounds (Xue et al., 2011; Omidvarborna et al., 2015b).

Conclusions are summarized as follows:

1. The FTIR spectra of biodiesel fuels obtained from SME, TO, and WCO showed the characteristic regions of oxygen bonds. Biodiesel fuels showed no sulfur peaks in their spectra, while no considerable absorbance peak was observed for ULSD due to the low concentration of sulfur. The presence of long carbon chains was verified by the vibration of C–H bonds. Although the results showed the difference in the degree of unsaturation among biodiesel fuels, the difference was not found very significant. The double bond peak for SME was 0.37% where the peaks for WCO and TO were about 0.34%.

2. After combustion of selected neat and blended fuels, all neat biodiesel fuels produced no soot particles. As the portion of biodiesel decreased in the blends, the amount of soot particles increased.

3. The size distribution of ULSD soot particles did not follow the same trend as other biodiesel fuels where they exhibited a quasi-monodispersed structure. The addition of biodiesel in blends reduces the inception of soot precursors, and in
addition it reduces the size and number of soot particles through further oxidation with extra oxygen included in biodiesel.

4. Elemental analysis on soot particles showed that under LTC only aluminum (Al), calcium (Ca), copper (Cu), iron (Fe), magnesium (Mg), molybdenum (Mo), sodium (Na), and potassium (P) can be detected from the combustion of ULSD and biodiesel fuels. It means other reported elements such as Zn and Cr possibly come from other external sources rather than fuel.

5. It was confirmed via FTIR analysis of soot particles that the extra oxygen content of biodiesel is thought to reduce the size of soot particles through enhanced oxidation, and it made the size distribution of soot particles narrower than ULSD.

6. According to the TGA analysis, the biodiesel blends were oxidized faster than ULSD. The blends of biodiesel fuels showed lower temperature peak than ULSD, which indicates faster soot particle oxidation. Among biodiesel fuels, WCO had the lowest temperature peak.

7. The laboratory results confirmed that the unsaturation degree is related to the oxygen content in biodiesel fuels. As unsaturation degree increased, the oxygen content in FAMEs increased. SME, the highly unsaturated biodiesel compared with WCO and TO, emitted smaller soot particles as shown in the TEM images. FTIR results showed the high degrees of unsaturation and high oxygen contents of biodiesel fuels.

The results presented here provide additional justification for the use of biodiesel as an alternative fuel, because biodiesel takes advantage of reduction of soot particles in addition to its value as a renewable energy source with low exhaust emissions.
3.5.3 Carbon Emissions

This study confirmed that the variation in the properties of the biodiesel led to the different carbon emissions over a range of combustion conditions. In this study, as the unsaturation degree increased, chain length increased and vice versa, therefore, the degree of unsaturation and chain length of FAMEs in biodiesel fuels are related and they are thought to be the causes for the results observed. Based on the presented results, the following conclusions can be drawn.

CO and CO$_2$ emissions are well correlated with the chemical characteristics of the fuels. The highest value of CO emissions and the lowest value of CO$_2$ emissions are observed for ULSD. For biodiesel fuels, the higher ratio of oxygen-to-carbon and shorter saturated chain length of methyl esters are thought to attribute to the more complete combustion and less CO and more CO$_2$ production compared to ULSD. More CO$_2$ was produced in the order of TO (the shortest and the most saturated), WCO, and SME (the longest and the least saturated). The CH$_4$ content in the emissions seemed to be enhanced by the addition of biodiesel in the blends. Saturated FAMEs with short chains such as in WCO and TO resulted in lower emissions of CH$_4$ than longer chains biodiesel fuels with unsaturated bonds.

Data provided in this study suggested biodiesel fuels with high levels of short FAMEs will have excellent characteristics with regard to CO, CO$_2$, and CH$_4$ emissions, especially in fuel-rich conditions and during incomplete combustion. Further studies are necessary to better understand the relations of the degree of unsaturation of FAMEs and biodiesel emissions.
Chapter Four

Field Experiments

Characterization of PM of public transit buses in idle modes has been conducted to identify PM specification and to determine the effect of biodiesel properties on the emissions. Two different sets of transit buses that were running on B20 were selected\(^1\).

4.1 Introduction

Biodiesel has received considerable attention for its potential as an alternative source of combustion fuel for the transportation sector. It was reported that it produces less PM, CO, HCs, and other air toxins than regular diesel, however, of these combustion products, PM emissions from biodiesel have been controversial (Omidvarborna et al., 2014). Compositions of the biodiesel PM may vary depending on temperature and the type of feedstocks, and the relation between PM characteristics and biodiesel combustion conditions is still to be clarified. Moreover, emissions from biodiesel during different stages of engine operation have not much investigated.

\(^1\) The content of this chapter is published as a paper entitled as: Omidvarborna, H., Kumar, A., and Kim, D.S. (2014). Characterization of particulate matter emitted from transit buses fueled with B20 in idle modes, Journal of Environmental Chemical Engineering 2, 2335-42.
4.1.1 PM Emissions

The early studies showed that PM size and concentration emitted from vehicles were dependent on engine operation conditions and fuel types. The major cause of PM generation in urban areas is attributed to the emissions from diesel-powered vehicles (Maricq et al., 2000; Kongtip et al., 2006). Although the total number of the transit buses may be small when compared with other vehicles, their emissions are counted as a significant source of total diesel PM in urban areas (EPA, 2002).

4.1.2 Elemental Emissions

Metal and inorganic elements such as iron, calcium, and sodium were reported to be originated from various sources in engines, but it is not practically possible to identify the major sources of elements found in PM in real systems. Elements of PM may be originated from multiple sources because the fuel charged in an engine contacts with various engine parts, oils, and lubricants. These contacts may affect the chemical compositions of PM emissions, and hence the toxicity level of them.

4.1.3 Positive Matrix Factorization (PMF) Study

PMF method is used to characterize the source apportionment of elements in PMs. PMF is a well-established and widely used method for source apportionment of atmospheric aerosols (Norris et al., 2008). It was successfully applied to datasets with a limited number of samples and to datasets with a limited number of species (Viana et al., 2008; Bhat and Kumar, 2013). PMF program developed by EPA (Norris et al., 2008), is a multivariate receptor model operating by minimizing the sum of the squared and scaled residuals (Q) in concentrations estimated as the sum of the products of factor profiles and contributions under a positivity constraint.
A chemically speciated data set can be viewed as a data matrix $X$ ($n$ by $m$ dimensions), in which $n$ is the number of samples and $m$ is the chemical species measured. The goal of multivariate receptor modeling, for example with PMF, is to identify a number of factors, $p$, the species profile, $f$, of each source, and the amount of mass, $g$, contributed by each factor to each individual sample. The relation of these variables is shown in Equation 4.1:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}$$  \hspace{1cm} (4.1)

where, $e_{ij}$ is the residual for each sample or species. PMF allows each data point to be individually weighed. This feature allows the analyst to adjust the influence of each data point, depending on the confidence in the measurement. The PMF minimizes the object function $Q$ (Equation 4.2), based upon uncertainty values as shown in Equation 4.2:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[ \frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^2$$  \hspace{1cm} (4.2)

More detail information regarding the model and parameters are presented elsewhere (Norris et al., 2008).

4.1.4 Elemental and Organic Carbon Emissions

Diesel exhaust particulates mainly consist of carbon that occupies a dominant portion (about 80-90%) of diesel PM concentration and mainly exists in the form of EC and OC (Rogge et al., 1993; Shandilya and Kumar, 2014). EC is non-volatile and strong light-absorbing carbon known as BC. It is a carbonaceous core of diesel PM and emitted during the combustion of fuels in the form of small, soot like particles often with other chemicals attached to its surface. OC is volatile and light scattering carbon, and its sources are found in traffic, industrial combustion and the degradation of carbon-containing materials. Both EC and OC contribute to the toxicity of diesel PM, and also
contribute to regional visibility impairment and climate change (Kim et al., 2006; Ramanathan et al., 2007).

Fuel type and composition and engine operating conditions have considerable effects on the emission of OC and EC (Gerald et al., 2010). Both EC and OC from biodiesel were observed to vary in a similar manner when these conditions change (Cheung et al., 2009; Lu et al., 2012; Shandilya and Kumar, 2014). Biodiesel combustion was reported to result in an increase in OC emissions and a decrease in EC emissions compared to regular diesel combustion. However, the EC/OC data for heavy duty engines in idle mode has never been fully developed and analyzed. A few OC/EC analyses on diesel engines fueled with biodiesel blends have been done in the past (Cheung et al., 2009; Zhang et al., 2011; Lu et al., 2012), but there is a lack of analyses on the effects of specific engine conditions on OC/EC generation (Cheung et al., 2009; Zhang et al., 2011; Lu et al., 2012; Shandilya and Kumar, 2013; Omidvarborna et al., 2014).

4.2 Objectives

Ten public transit buses run on a biodiesel blend were selected to perform the characterization of PM. Emission samples were collected in both hot and cold idle mode from these buses operating in Toledo, Ohio. At the time of PM sampling, B20 was used as fuel to characterize PM emissions collected from the exhaust with our database. Characterizations of PM, elemental analyses, source apportionment, EC and OC were performed and the data will be compared with the published data. Moreover, PMs from engines with different ages and hot/cold idle modes were compared with samples obtained from the study of Shandilya and Kumar (2013 and 2014).
4.3 Methodology

Two sets of transit buses (each set contains five on-road buses) from TARTA running on B20 were selected for both hot and cold idle tests (e.g., minimum load, acceleration at the speed of zero). A constant volume flow rate of emissions has been assumed in the calculations for the exhaust flow rate (Lim, 2002).

The hot idle test means collecting samples during the night time when the buses arrive back at the garage from a regular route, and the cold idle test means collecting samples in the morning before the buses leave the garage. To avoid the influence of existing PM inside the garage on the samples, the sampling was conducted outside the garage in an open area. Sampling was done by CatchCan (Shandilya and Kumar, 2014) which was used directly on the tip of exhaust pipe to capture PM. The exhaust flow rate data was obtained and calculated at a maximum rpm, and thereby it can be easily compared with part of the previous results (Shandilya and Kumar, 2013). Table 4.1 summarizes the main engine parameters for the three different series. At the time of sampling, two bus series, 500 and 700, were 10 years old, whereas the third one (800 series) was 3 year old and equipped with EGR. Engine capacity and maximum power of 500 series were lower than the other two series, 700 and 800.
Table 4.1. Specification of tested transit buses (main engine parameters)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>MBE900 Mercedes Benz</td>
<td>Thomas</td>
<td>2003</td>
<td>28,580</td>
<td>7.2L</td>
<td>260HP</td>
<td>800 ft-lbs @ 1200 RPM</td>
<td>2007 2</td>
</tr>
<tr>
<td>700</td>
<td>Cummins ISL6LTA</td>
<td>Gillig</td>
<td>2003</td>
<td>39,000</td>
<td>8.9L</td>
<td>289HP @ 2000 RPM</td>
<td>900 ft-lbs @ 1300 RPM</td>
<td>2007 5</td>
</tr>
<tr>
<td>800</td>
<td>Cummins ISL-07</td>
<td>Eldorado National</td>
<td>2010</td>
<td>42,760</td>
<td>8.9L</td>
<td>280HP @ 2200 RPM</td>
<td>900 ft-lbs @ 1300 RPM</td>
<td>2007 5</td>
</tr>
</tbody>
</table>

The collection time for PM was 15 min, which was similar to the previous study (Shandilya and Kumar, 2013). Because of the high exhaust temperature and the collecting method which directly captures PM at the tip of the exhaust pipe, effects of ambient temperature and humidity were assumed to be negligible.

Quartz filter papers were used for collecting PM samples (Figure 4.1). The PM masses were determined gravimetrically by subtracting the final mass of a quartz filter paper from the initial mass of the sample filter. The steps of pre-treatment and post-treatment for the gravimetric mass determinations were described as follows: The filters were incubated in an incubator at 20 °C and relative humidity of 50% for 24 hours (40 Code of Federal Regulations recommends 1-80 hours) before weighing and after weighing. A certified Mettler Toledo XP105 microbalance (maximum capacity: 31 g/120 g, accuracy: 0.01 mg/0.1 mg), which was placed on a vibration-free table, was used for weighing the filter papers.
RTI Laboratories Inc. in North Carolina carried out EC and OC analyses on PM collected on filter papers using Interagency Monitoring of Protected Visual Environments A (IMPROVE_A) method. In this method, seven carbon fractions were defined including OC1 – OC4, and EC1 – EC3. The first four fractions, OC1 – OC4, were determined at 140°C, 280°C, 480°C and 580°C in a helium atmosphere, respectively. The other three fractions, EC1, EC2, and EC3, were determined in 2% oxygen and 98% helium atmosphere at 580°C, 740°C, and 840°C, respectively (Shandilya and Kumar, 2014).

ICP-OES was used to evaluate elemental composition of PM at the USDA laboratory, at the University of Toledo. The results of elemental analysis were interpreted by using PMF model (Cheng et al., 2003; Zhang et al., 2004). PMF has been used extensively as a means of source apportionment (Kim et al., 2004; Lee et al., 2006; Pekney et al., 2006; Song et al., 2007; Bhat and Kumar, 2013). In this study, for the first time, PMF was used to determine the source apportionment for elements of PM which were emitted from transit buses in hot and cold idle modes.

Figure 4.1. PM samples on quartz filter papers after (left) and before (right) sampling.
4.4 Results and Discussion

As shown in Table 4.1, the ten transit buses powered by Cummins engines were tested in this study, and the results were compared with the literature data. No modifications in the engines or fueling systems were made on the TARTA vehicles to run on biodiesel.

4.4.1 PM Emission Analyses

Table 4.2 shows the results of several samples (PM concentration per unit volume of the exhaust flow rate) from 500, 700 and 800 series fueled with B20 in two idle modes. A complete analysis was done first by choosing a large population of different on-road buses running on B20. Five buses in two different series were selected for PM analyses. The test results with very narrow error ranges proved the credibility of the PM emissions testing conducted in this study. The results were compared with a previous study performed on 500 series (Shandilya and Kumar, 2013), in which the authors investigated two buses that ran on both B20 and ULSD. It is worth mentioning that since then, all TARTA transit bus fuels were shifted to B20 and none of them has used ULSD, therefore, the results obtained in this study only address B20 emissions. As shown in Table 4.2, the difference between B20 and ULSD emissions in 500 bus series is very distinct and clearly shows the dependency of PM on the engine operating mode and fuel type. For all the engines tested under hot and cold idle modes, B20 produced less PM than ULSD. PM generated through combustion can get further oxidized due to higher oxygen content of biodiesel. Thus, reduction of the particle size and the number of accumulation of fine particles is observed for B20 compared with ULSD fuel.
Furthermore, the higher viscosity and density of biodiesel compared to ULSD are thought to possibly contribute to the reduction in PM emissions because it may lead to an increase in the injection pressure that enhances uniform distribution of fuel in an engine (Betha and Balasubramanian, 2011). In 500 series experiments, buses running in hot idle mode emitted PM in substantially higher concentrations than the ones in cold idle mode while the lowest PM concentration was observed for B20 cold idle testing. B20 hot idle and ULSD cold idle data had a lower, wider peak around the mean and thinner tails which are called platykurtotic (Shandilya and Kumar, 2013). The PM emissions during the hot idling were greater than those in cold idle mode because of the increase in the temperature as described by Wang et al. (2000). These results can be explained based on the fact that the majority of PM is originated from soot which is usually formed in fuel-rich or low-oxygen regions of a diesel engine at elevated temperatures (Shandilya and Kumar, 2013). 700 (10 years old at the time of sampling) and 800 (3 years old) series produced two orders of magnitude less PM than the 10 year old 500 series during both hot and cold idle modes. The difference of PM between hot and cold idle modes was greater for 500 series than for the other two series. On average, 700 and 800 series showed more than 98% improvement in PM formation than 500 series. Although both

### Table 4.2. Comparison for PM (µg/m³) for three different transit series fueled with ULSD and B20.

<table>
<thead>
<tr>
<th></th>
<th>500 series (Shandilya and Kumar, 2013)</th>
<th>700 series</th>
<th>800 series</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ULSD</td>
<td>B20</td>
<td>B20</td>
</tr>
<tr>
<td></td>
<td>Hot</td>
<td>Cold</td>
<td>Hot</td>
</tr>
<tr>
<td>Mean</td>
<td>215.60±33.40</td>
<td>209.80±33.00</td>
<td>1.56±0.79</td>
</tr>
<tr>
<td>Min.</td>
<td>149.67</td>
<td>164.49</td>
<td>0.38</td>
</tr>
<tr>
<td>Max.</td>
<td>247.49</td>
<td>249.57</td>
<td>2.77</td>
</tr>
<tr>
<td>No. of samples</td>
<td>7</td>
<td>7</td>
<td>20</td>
</tr>
</tbody>
</table>

* Results presented here are for five buses in both 700 and 800 series.
700 and 500 series engines are 10 years old, 700 series produced less PM than 500 series, which indicates the engine type is more important than age in PM production. In cold idle mode, the PM range was found between 0.42 and 5.59 mg/m³ for 700 series and 0.01–0.98 mg/m³ for 800 series. The trend is the same for hot idling as well, which was 0.38–2.77 mg/m³ for 700 series and 0.42–0.70 mg/m³ for 800 series. 700 series showed a slightly more PM in cold idle mode than hot idle mode, but considering the standard deviation with 95 confidence level, the difference is not significant. The lowest PM emission from the 800 series is thought to be due to the EGR effect. Previous studies showed that the use of the biodiesel blends with a post-treatment technology had reductions of 50–80% in PM compared to the emissions with the diesel fuel without it (Bagley et al., 1998). As stated above, the low PM emissions from biodiesel is thought to be due to the characteristics of biodiesel, such as higher oxygen content and higher viscosity of biodiesel than ULSD (Leung et al., 2006; Tsolakis et al., 2007; Tsai et al., 2010). Cheung et al. (2009) suggested that the oxygen content of biodiesel inhibits in-cylinder soot production by disrupting the carbon chain development and promoting oxidation. On the other hand, the high oxygen content of B20 intensifies soot oxidation and finally reduces the mass of soot product. Soot oxidation is the sum of the processes that reduce the mass of soot and convert the solid soot particles back into gas (e.g., CO and CO₂). Oxidation is similar to surface growth in the sense that the surface area of the particles affects the rate of oxidation. Unlike the surface growth of soot, which occurs in a specific step, oxidation happens all the time during and after soot formation. In addition, fuel property such as viscosity, may have an effect on engine operation (e.g., injection timing). This fuel property effect on soot production needs to be more
investigated in real engine studies. Low sulfur content of biodiesel and absence of aromatic compounds are also thought to be the other reasons for PM mass reduction (Shandilya and Kumar, 2009; Tsai et al., 2010). Some of the parameters, such as engine speed and load that influence the PM emission from diesel engines were not considered because the tests were done in idle modes. In idle mode the engine speed was zero and load was kept at below 10% in all the experiments performed in this study. For real-world driving experiments, those parameters are very important to consider. When these parameters are included under real-world driving conditions, it is expected that PM emission will be much higher than in idle modes.

4.4.2 Elemental Emission Analyses
Elemental analysis was conducted to better understand the health effects associated with PM emissions, and to develop a relationship between the PM chemical structure and the origins of the particles. The concentrations of Al, Ca, Cr, Cu, Fe, Pb, Mg, Mo, Ni, P, K, Si, Na, S, and Zn in PM were determined for all the samples using ICP–OES. All the comparisons made for the tested series are shown in Table 4.3. The results indicate that there were some metals such as Mo and Ni found in 500 series and not found in 700 and 800 series. Likewise, some other metals, such as Cr and Si, were found in hot idle mode and not found in cold idle mode. Ca, Fe, and Si were reported as the three most-abundant elements for ULSD (an average of 84% of mass) in public transit buses, whereas Ca, Fe, Mg, P, Si, and Zn were observed as the most-abundant elements for B20 (an average of 96% of mass) in the 500 bus series in cold idle mode (Shandilya and Kumar, 2013).
Table 4.3. Average PM elemental composition (ng/m$^3$) collected from tail pipe emission of TARTA buses.

<table>
<thead>
<tr>
<th></th>
<th>500 series *</th>
<th>700 series</th>
<th>800 series</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ULSD B20</td>
<td>Cold Idling B20</td>
<td>Hot Idling B20</td>
</tr>
<tr>
<td>Aluminum (Al)</td>
<td>8.1 16.2</td>
<td>5.150±12.840</td>
<td>3.930±6.010</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>165.4 215.5</td>
<td>335.570±165.700</td>
<td>97.680±35.650</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>0.4 0.7</td>
<td>ND</td>
<td>1.110±2.560</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>0.9 2.6</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>36.8 48.5</td>
<td>34.630±28.060</td>
<td>33.910±17.270</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>0.7 1.3</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>ND 86.1</td>
<td>28.270±16.770</td>
<td>3.400±4.890</td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>1.3 3.2</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>1.3 5.2</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Phosphorus (P)</td>
<td>32.6 60.7</td>
<td>3.320±8.650</td>
<td>4.340±4.710</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>ND ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>200.5 284.2</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>NR NR</td>
<td>9.140±19.320</td>
<td>183.600±14.140</td>
</tr>
<tr>
<td>Sulfur (S)</td>
<td>NR NR</td>
<td>21.650±16.680</td>
<td>32.590±3.660</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>29.4 71.1</td>
<td>8.020±10.710</td>
<td>11.010±6.190</td>
</tr>
<tr>
<td>#</td>
<td>NR NR</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

NR: Not Reported by the author.
ND: Not Detected (Concentration below the quantitation limit).
* Collected and measured for only cold idling mode (Shandilya and Kumar, 2013).

It was observed that Ca was the most-abundant element in cold idle mode; for 700 series the average mass of Ca was 76%, and it was 82% for the 800 series. On the other hand, for the hot idle test, the dominant elements were observed Na and Ca with 71% in mass for 700 series and 72% for the 800 series. It can be seen that the collected samples from the tail pipe emissions contained significantly more Ca than the other elements. Ca is reported as a typical marker for exhaust emissions in various engine types (Lough et al., 2005; Agarwal et al., 2011a). The higher values of Ca may be attributed to various sources like wear in bushings, injector shields, coolant core tubes, thrust washers, valve guides, connecting rods, piston rings, bearings, sleeves, bearing cages, detergent additives or even dust (Cadle et al., 1999; Agarwal et al., 2011a; Shandilya and Kumar, 2013; Omidvarborna et al., 2014). Ca was also found (Agarwal et al., 2011a) in abundance in
diesel (902.3 mg/g), biodiesel (721.2 mg/g) and lubricating oil (2046.8 mg/g). The possible sources of sodium (Na) could be specific additives in lubricant oil (Sharma and Maloo, 2005). The values of Na in hot idling were observed higher than that of cold idling, and its concentration was the highest compared to all the other metals in hot idling. Higher engine temperature is thought to be the main reason for releasing more Na in hot idle mode. Fe, Mg and S were detected in high concentrations (15–19 wt%) in cold idle mode. Also Fe, S, and Si were observed in hot idle mode with 23–24 wt%. Possible sources of iron (Fe) are rust and wear of mechanical parts, such as engine block, cylinder, gears, cylinder liners, valve guides, wrist pines, rings, camshaft, oil pump, crankshaft, ball and roller bearings (Cadle et al., 1999; Totten et al., 2003; Agarwal et al., 2011a). It also might be contributed by dust. Note that diesel inherently has 402.3 mg/g, biodiesel has 419.8 mg/g and lubricant oil has 827.0 mg/g of irons in the fuel (Lough et al., 2005). Magnesium (Mg) is thought to come from engine parts, and fuel additives including cylinder liner, gear box housings and detergent inhibitors. Sulfur (S) is generated from wear of the engine block, cylinder, gears, cylinder liners, valve guides, wrist pines, rings, camshaft, oil pump, crankshaft, ball and roller bearings, rust for iron and a little amount of sulfur (<15 ppm) in ULSD. Silicon (Si) is thought to come from dirt intruded from a dirty air cleaner or seal materials. Si was found in high concentration in 500 series in cold idle and not found in 700 and 800 series in the same mode. The Si concentrations in PM collected from the exhaust of the ULSD fueled buses were higher than the concentrations in PM collected from the exhaust of the biodiesel fueled buses. Sulfur (S) plays an important role in the self-lubricating properties of diesel, hence for ULSD, the wear-generated metal concentrations would be possibly even higher than regular diesel.
Figure 4.2. Elemental analysis for 700 and 800 bus series in both cold and hot idle modes.

Figure 4.2 represents the box plots of elemental analysis for two transit bus series (700 and 800 series) run on B20 in cold and hot idle modes. The most-abundant element in cold mode is Ca, and 800 series produced almost an order of magnitude higher Ca than 700 series in cold idle mode. The differences in Ca between hot and cold idle modes were also an order of magnitude in both 700 and 800 series.

Mo, Ni, Pb and Cu that were found in 500 series, were not detected here. The higher values of Si and Cr in hot idling than in cold idling are thought to be due to the high temperature of the engine. For the P concentration, 500 series’ (both running on ULSD and B20) exhaust particulates showed relatively high levels of P concentration, where 700 series showed trace concentrations of P in the particulates. However, 800
series displays no P concentration in elemental analysis. Given that both 500 (Mercedes) and 700 (Cummins) series were 10 years old, and 800 series (Cummins) was 3 years old at the time of sampling, the difference in P between the tested buses does not seem to come from the wear and tear of engine because the 10-year old 700 series produced much lower P than 500 series of the same age. Most phosphorus in diesel emissions is known to come from the anti-wear and anti-rusting agents (Sharma and Maloo, 2005). The source identification data for other common trace elements is available elsewhere (Sharma and Maloo, 2005).

4.4.3 PMF Results
PMF was used to elucidate sources of PM elements collected in TARTA garage. The determination of the appropriate number of factors and the interpretation of the factor profiles with respect to a reasonable physical meaning is one of the most critical parts in the application of PMF. For the source apportionment, the detected elements from elemental analyses were used as an input to PMF. Determining the number of factors is one of the major difficulties in factor analysis. In this study, the number of resolved source profiles was four where a good fit of the predicted concentrations to the measured values was obtained. The numbers of runs and seed counts were kept the same as default values. Figure 4.3 summarizes the source apportionment results produced by PMF3 software obtained from the elemental analysis of collected PM from the TARTA buses in two idle modes. The analysis was performed by using the uncertainties of individual elements obtained from a study comparing the accuracy and precision of the results obtained by ICP–OES analysis techniques. Tentative source names were assigned to factors based on known chemical signatures measured during source tests. Four factors were identified as fuel, oil and lubricants, engine parts and ambient media. Factor 1 (fuel)
accounts for the majority of S in PM. The sulfur content mainly comes from ULSD fuel which has less than 15 ppm of sulfur. Figure 4.3 shows that the fuel source significantly contributed to the emissions of sulfur (S) in cold idle mode (85.70% for 700 and 50.50% for 800 series). Factor 2 which represents oil and lubricants, accounts for the majority of Mg, P, and Ca in the PM exhaust. Oil and lubricants were the major contributors for magnesium emission in cold idle mode. It is noted that oil and lubricants were responsible for zinc emission (70.80%) from the hot idling 700 series whereas no significant zinc was found in other conditions. Calcium (Ca) in 700 H and 800 H emissions mostly came from oil and lubricants (43.50% and 57.70%, respectively). Likewise, most phosphorus (P) in 700 H (94.30%) sample comes from oil and lubricants. For 800 C, magnesium (Mg) also comes from oil and lubricants (84.90%). Factor 3 (engine parts) contained the highest measured contribution of Fe along with minority of other elements. As stated before, engine parts were the largest contributor for iron (Fe) emission in both cold and hot idle modes. In general, most Ca (65.20% and 63.30% for 700 C and 800 C, respectively) and Al (70.70% for 800 H) came from ambient air (factor 4) indicating that dust got into a storage tank (Shandilya and Kumar, 2013; Omidvarborna et al., 2014). Ca is reported from other references as a marker for diesel and biodiesel fuels as well (Agarwal et al., 2011a). While herein, the results clearly show that Ca is unique marker for biodiesel studies.
### 700 SERIES IN COLD IDLE MODE

(a)

<table>
<thead>
<tr>
<th>Contribution (%)</th>
<th>Calcium</th>
<th>Iron</th>
<th>Magnesium</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient air</td>
<td>65.2</td>
<td>0.7</td>
<td>15.2</td>
<td>12.8</td>
</tr>
<tr>
<td>Engine parts</td>
<td>9.0</td>
<td>83.2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Oil and lubricants</td>
<td>7.3</td>
<td>2.0</td>
<td>84.8</td>
<td>1.5</td>
</tr>
<tr>
<td>Fuel</td>
<td>18.5</td>
<td>14.2</td>
<td>0.0</td>
<td>85.7</td>
</tr>
</tbody>
</table>

### 700 SERIES IN HOT IDLE MODE

(b)

<table>
<thead>
<tr>
<th>Contribution (%)</th>
<th>Calcium</th>
<th>Iron</th>
<th>Sodium</th>
<th>Phosphorus</th>
<th>Sulfur</th>
<th>Silicon</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient air</td>
<td>24.5</td>
<td>0.0</td>
<td>17.4</td>
<td>0.0</td>
<td>20.0</td>
<td>36.5</td>
<td>29.2</td>
</tr>
<tr>
<td>Engine parts</td>
<td>9.4</td>
<td>55.4</td>
<td>38.1</td>
<td>0.0</td>
<td>33.3</td>
<td>38.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Oil and lubricants</td>
<td>43.5</td>
<td>44.6</td>
<td>0.4</td>
<td>94.3</td>
<td>11.5</td>
<td>0.0</td>
<td>70.8</td>
</tr>
<tr>
<td>Fuel</td>
<td>22.5</td>
<td>0.0</td>
<td>44.1</td>
<td>5.7</td>
<td>35.3</td>
<td>25.3</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Figure 4.3. Percent contribution of four common sources in PM elemental analysis (a) 700 series in cold idle mode (b) 700 series in hot idle mode (c) 800 series in cold idle mode (d) 800 series in hot idle mode.
4.4.4 Elemental and Organic Carbon Emission Analyses

The average EC and OC emissions in the collected PM for two different bus series and two idle modes with low engine loads are shown in Figure 4.4. Detailed values of carbon emissions are presented in Table 4.4. The results on both ULSD and biodiesel show that EC emitted at much lower values than OC. Biodiesel and ULSD emissions analyses indicate that both fuels could effectively reduce the emission of EC. According to Figure 4.4(a), it can be seen that EC (EC1 + EC2 + EC3) was reduced to less than 10% by switching from 700 to 800 series at idling conditions, while OC gradually increased to 90% at minimum load (<10%). The values of EC1, EC2, and EC3 for 800 series in both cold and hot idling showed the same values and ratios. For 700 series, however, more EC was released during hot idling compared to cold idle mode. The maximum amount of observed EC in this case was reported 35% of total carbon (TC = EC + OC). Additionally Figure 4.4(b) and (c) shows the concentrations of elemental and organic carbon by transmittance and reflectance in collected samples. These ratios agree well with the OC/EC ratios in Figure 4.4(a).

Table 4.4. Carbon emissions from transit buses in three different bus series.

<table>
<thead>
<tr>
<th>(µgC/m³)</th>
<th>OC</th>
<th>EC</th>
<th>TC</th>
<th>OC1</th>
<th>OC2</th>
<th>OC3</th>
<th>OC4</th>
<th>EC1</th>
<th>EC2</th>
<th>EC3</th>
</tr>
</thead>
<tbody>
<tr>
<td>700_C_BD</td>
<td>5.91</td>
<td>1.29</td>
<td>7.20</td>
<td>0.05</td>
<td>4.05</td>
<td>1.46</td>
<td>0.35</td>
<td>0.51</td>
<td>0.76</td>
<td>0.02</td>
</tr>
<tr>
<td>700_H_BD</td>
<td>1.49</td>
<td>0.80</td>
<td>2.29</td>
<td>0.09</td>
<td>0.72</td>
<td>0.51</td>
<td>0.17</td>
<td>0.26</td>
<td>0.53</td>
<td>0.01</td>
</tr>
<tr>
<td>800_C_BD</td>
<td>4.25</td>
<td>0.32</td>
<td>4.57</td>
<td>0.46</td>
<td>1.24</td>
<td>1.92</td>
<td>0.63</td>
<td>0.27</td>
<td>0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>800_H_BD</td>
<td>3.61</td>
<td>0.38</td>
<td>3.99</td>
<td>0.83</td>
<td>1.24</td>
<td>1.07</td>
<td>0.47</td>
<td>0.27</td>
<td>0.11</td>
<td>0.00</td>
</tr>
<tr>
<td>500_H_ULSD</td>
<td>99.89</td>
<td>13.71</td>
<td>113.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500_C_ULSD</td>
<td>87.73</td>
<td>22.46</td>
<td>110.19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500_H_BD</td>
<td>145.25</td>
<td>10.68</td>
<td>155.93</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500_C_BD</td>
<td>73.81</td>
<td>13.46</td>
<td>87.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Average values are reported here.
** Data for 500 bus series were reported in Shandilya and Kumar (2014).

Furthermore, the results in Figure 4.4 suggest that an increase in temperature increases the proportion of EC in 700 series. This temperature effect did not show for 800
series because they were equipped with a post-treatment system, and thereby the temperature difference between the hot and cold idle modes showed small (or no) change in OC/EC ratios. The reason for the greater increase of EC over OC during hot idling may be explained that because EC is known to be formed in the fuel-rich zone under high pressure and temperature. Therefore, hot idling should be avoided to reduce EC emissions. Carbon stored in the form of EC1, OC1 and OC2. EC1 (called char-EC) is formed directly from pyrolysis of fuel at relatively low temperature and EC2 + EC3 (or soot-EC) could be regarded as the trace composition in diesel emissions. The OC1 and OC2 fractions dominated the freshly emitted exhaust, while OC3 and OC4 were minor fractions. These ratios are important in conducting the aging studies of the diesel exhaust (Viana et al., 2008). The OC1–OC4, and EC1–EC3 emissions as well as OC, EC, and TC are present in Table 4.4. As shown in this table, carbonaceous emissions from both 700 and 800 series were significantly lower than the previous study on 500 series (Shandilya and Kumar, 2014). Shandilya and Kumar (2014) reported that for ULSD-fueled buses, EC2 was the major exhaust of regular diesel vehicles (32.50% of total carbon (TC)) and OC2 was the major exhaust emissions for biodiesel fueled buses (42.70% of TC). In this present study, the results appear to agree well with the report in Shandilya and Kumar (2014), especially for 700 series in both hot (31.40% of TC) and cold (56.25% of TC) idling. It can be inferred that biodiesel as a fuel successfully eliminates the toxic component of EC in emissions. It is thought that the reduction of EC in biodiesel emissions is primarily due to the presence of oxygen in the fuel.
4.4 Conclusion

PM emissions from transit buses running on ULSD and soybean biodiesel (B20) were investigated. The results of the PM emission analysis show that PM emissions were dependent on the engine model, cold and hot idle modes, and fuel type. The emission characteristics of biodiesel were analyzed in terms of PM, elemental analyses, and OC/EC analyses. The results showed that the PM was related to idle conditions. The number of heavy metals in PM emitted during hot idling was greater than those from cold idling. Elemental analysis was used to find the sources of PM formation. PMF was used for source apportionment of PM collected from tail pipe emissions. Four factors were
obtained and identified as the possible sources: fuel, oil and lubricants, engine parts, and ambient air. The most-repeatable elements in all cases were Ca, Fe, and S. The carbon speciation of PM from transit buses in idle mode (both cold and hot) were evaluated in this study and compared with literature data. The results indicated that the use of biodiesel could effectively reduce EC and increase the portion of OC emission by 10% and even by 90% in some cases. Using biodiesel in transit buses may decrease the proportion of EC, which is more toxic than OC. Hot idling appeared to produce more EC, and therefore it should be avoided. The main reasons for PM reduction in biodiesel emissions are thought to be due to the oxygenated structure of biodiesel fuel, engine technology, and the presence of EGR in the system.
Chapter Five

ANN Modeling Study

The purpose of this study is to experimentally analyze the NOx emissions from transit buses operating in idle mode on a blend of biodiesel fuel with the aid of ANN. To acquire data for training and testing the proposed ANN, two different series of urban transit buses are tested. To compare NOx emissions, one set is equipped with EGR and the other one is not. NOx emissions will be compared with recorded variables stored from engine data and finally will be modeled with the aid of ANN\(^1\).

5.1 Introduction

Generally, biodiesel fuels are known to offer reduction of harmful pollutant emissions, but it produces higher NOx emissions than ULSD. A number of attempts have been made to reduce NOx emissions from diesel and biodiesel engines with various combustion modification methods (Abd-Alla, 2002; Szybist et al., 2007; Saleh, 2009). EGR has been proved to be a very effective and practical NOx reduction technique (Agrawal et al., 2004; Zheng et al., 2004; Taghavifar et al., 2014). EGR in diesel combustion reduces exhaust emissions essentially by lowering the peak combustion

\(^1\) The content of this chapter is accepted for publication as a paper entitled “Artificial Neural Network (ANN) prediction of NOx emissions from EGR and non-EGR engines running on soybean biodiesel fuel (B5) during cold idle mode” in Environmental Progress & Sustainable Energy. doi:10.1002/ep.12376
temperature, using diluent gases of high specific heat (containing substantial levels of 
H$_2$O and CO$_2$), and low oxygen level in the cylinder (Hountalas et al., 2008; Agarwal et 
al., 2011b).

ANN is a powerful modeling technique with the ability of identifying highly 
nonlinear and complex systems that can make them simpler than other approaches (Adi et 
al., 2009; Obodeh and Ajuwa, 2009; Kiani et al., 2010). In this study, ANN is used to 
predict NOx emissions from two engines, one equipped with an EGR system and the 
other one without it. Both engines are run on a B5 blend of soybean biodiesel in cold idle 
mode. Due to biodiesel fuel price, TARTA has changed its policy regarding fuels’ blend 
(from B20 to B5). This modeling technique can be applied to estimate the desired output 
parameters when enough experimental data is provided.

5.2 Objectives

From the literature it is observed that not many studies have been carried out on 
idle mode emissions. To the best of our knowledge, there is no literature that reports the 
application of ANN to predict and model NOx emissions in terms of EGR and cold idle 
mode. Furthermore, few investigations have been carried out with ANN and EGR 
combination for the engines under loads. Hence, the current investigation is carried out to 
analyze the effect of EGR and non-EGR engine on NOx emissions in urban transit buses 
running on B5 in cold idle mode.

5.3 Experimental Setup and Procedure

An experimental investigation was carried out on existing transit buses operated 
by TARTA in the city of Toledo, Ohio. Both SME biodiesel and ULSD were purchased
from local providers and blended in a reservoir provided by TARTA. The properties of ULSD and SME fuel are provided in chapter three. 700 series referred to those buses which are not equipped with EGR, while 800 series are equipped with EGR. The non-EGR engine was 11 years old, whereas the EGR engine was 4 years old at the time of study. The experiment was done from September to October 2014. Table 5.1 summarizes the main engine parameters for the two different engines. Although the engines were manufactured in different years, the engine capacity, maximum power, and maximum torque of them were almost the same. Experimental investigation of NOx emissions was conducted on two different urban transit buses operating with B5 fuel.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Engine</th>
<th>Yr. of Mfg.</th>
<th>Gross weight (lbs)</th>
<th>Engine capacity</th>
<th>Maximum power @ RPM</th>
<th>Maximum torque @ RPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-EGR</td>
<td>Cummins ISL6LTAA</td>
<td>2003</td>
<td>39,000</td>
<td>8.9L</td>
<td>289HP @ 2000 RPM</td>
<td>900 ft-lbs @ 1300 RPM</td>
</tr>
<tr>
<td>EGR</td>
<td>Cummins ISL-07</td>
<td>2010</td>
<td>42,760</td>
<td>8.9L</td>
<td>280HP @ 2200 RPM</td>
<td>900 ft-lbs @ 1300 RPM</td>
</tr>
</tbody>
</table>

The NOx analyzer was directly attached at the tip of exhaust pipes to capture NOx emissions continuously. As shown in Figure 5.1, sampling was conducted outside the garage in an open area during idling before the buses left for the daily routine (cold idle). The engines were connected to the data acquisition systems provided by Cummins, so that several operating parameters could be simultaneously measured. The main specifications of the NOx gas analyzer are given in chapter three.
ANN Modeling Approaches

Neural networks are a type of artificial intelligence system that simulates the way the neurons work in the human brain. Neurons, which can learn from examples, are able to deal with nonlinear problems, and, once trained, they can perform prediction and generalization. In the present work, variable parameters that influence on exhaust emissions (Hountalas et al., 2008; Maiboom et al., 2008) such as time, fuel temperature, intake air temperature, and percent fuel for non-EGR engine (4 inputs) are considered for NOx modeling. For the EGR engine, time, catalyst intake temperature after treatment, the diesel particulate filter intake/outlet temperature after treatment, EGR temperature, fuel flow rate, and the intake air temperature are implemented (7 inputs). The output of the system will be the concentration of NOx from the each engine. Engine load is one of the most important parameters affecting engine performance and exhaust emissions (Marques et al., 2007; Kumar et al., 2004). In idle mode, engine load is kept at 10% and engine speed remained at 1000 rpm. Therefore, the load percent and engine speed are not considered as input variables.
Table 5.2. Measured/calculated statistical engine data including NOx with respect to the four input parameters in a non-EGR engine

<table>
<thead>
<tr>
<th>Input (non-EGR engine)</th>
<th>Min</th>
<th>Max</th>
<th>Avg.</th>
<th>Median</th>
<th>Mode</th>
<th>Std. deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel temperature</td>
<td>52.1</td>
<td>81.2</td>
<td>68.6</td>
<td>69.7</td>
<td>77.9</td>
<td>8.7</td>
</tr>
<tr>
<td>Intake manifold temp.</td>
<td>49.8</td>
<td>55.6</td>
<td>53.2</td>
<td>53.4</td>
<td>53.7</td>
<td>1.6</td>
</tr>
<tr>
<td>Percent fuel</td>
<td>5.3</td>
<td>13.1</td>
<td>7.6</td>
<td>7.0</td>
<td>6.9</td>
<td>1.8</td>
</tr>
<tr>
<td>NOx</td>
<td>217.0</td>
<td>1208.0</td>
<td>571.6</td>
<td>526.0</td>
<td>479.0</td>
<td>149.0</td>
</tr>
</tbody>
</table>

Diesel particulate parameters (oxidation catalyst temperature and particulate intake/outlet temperature) in the EGR engine are incorporated in NOx modeling because the engine exhaust gas including NOx, is used for regeneration process either continuously or periodically during thermal regeneration. During this process, exhaust gas including NOx and unreacted O$_2$ react with trapped soot particles and produce mainly CO$_2$.

Table 5.3. Measured/calculated statistical engine data including NOx with respect to the seven input parameters in an EGR engine

<table>
<thead>
<tr>
<th>Input (EGR engine)</th>
<th>Min</th>
<th>Max</th>
<th>Avg.</th>
<th>Median</th>
<th>Mode</th>
<th>Std. deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>After treatment diesel oxidation catalyst temp.</td>
<td>190.3</td>
<td>232.1</td>
<td>226.2</td>
<td>229.4</td>
<td>230.5</td>
<td>8.4</td>
</tr>
<tr>
<td>After treatment diesel particulate filter temp.</td>
<td>163.6</td>
<td>219.4</td>
<td>210.4</td>
<td>217.0</td>
<td>218.0</td>
<td>13.7</td>
</tr>
<tr>
<td>After treatment diesel particulate filter out.</td>
<td>88.1</td>
<td>206.0</td>
<td>169.1</td>
<td>181.5</td>
<td>202.4</td>
<td>35.0</td>
</tr>
<tr>
<td>EGR temp.</td>
<td>82.1</td>
<td>131.2</td>
<td>109.1</td>
<td>107.2</td>
<td>106.6</td>
<td>13.8</td>
</tr>
<tr>
<td>Fuel flow rate commanded</td>
<td>1.6</td>
<td>3.2</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Intake manifold temp.</td>
<td>67.4</td>
<td>87.6</td>
<td>77.2</td>
<td>78.7</td>
<td>67.4</td>
<td>6.1</td>
</tr>
<tr>
<td>NOx</td>
<td>80.0</td>
<td>659.0</td>
<td>106.8</td>
<td>108.0</td>
<td>118.0</td>
<td>35.1</td>
</tr>
</tbody>
</table>

Initially independent models are developed for the both engines because they had different inputs variables. For the non-EGR and EGR engines, out of more than 1500 data points, 70% will be used in the training set, 15% for the validation set, and the remaining 15% will be employed for testing for the both models. The range of variations of the operating parameters and the corresponding values of NOx emissions are listed in Tables
5.2 and 5.3 together with their statistical parameters (including minimum, maximum, average, median, mode, and standard deviation), respectively.

Achieving an optimal ANN structure is an essential part of neural network study in order to harness the maximum advantage of the computational intelligence of the network. The neural network toolbox of MATLAB 8.0.1 is used to form the ANN model. A simple structure of the ANN model is shown in Figure 5.2. The word network in the term ANN refers to the inter–connections between the neurons in the different layers of each system. An example system has three layers. The first layer has input neurons which send data via synapses to the second layer of neurons, and then via more synapses to the third layer of output neurons. More complex systems will have more layers of neurons, some having increased layers of input neurons and output neurons. The synapses store parameters called "weights" that manipulate the data in the calculations (Najafi et al., 2009; Yusaf et al., 2010). Operating parameters of the engines are fed into the network as inputs and the NOx emissions came out of the network as outputs. The network is trained using LM training algorithm (trainlm) to find the optimum number of neurons in the hidden layer for which the error was minimum (Roweis, 2004; Taghavifar et al., 2014). The activation function for the hidden layer is selected to be logsig (Ghobadian et al., 2009; Kiani et al., 2010; Yusaf et al., 2010).
5.5 Results and Conclusion

5.5.1 Experimental Results

As pointed out earlier, one of the most critical emissions from the engines is NOx. In combustion of biodiesel fuels, the formation of NOx is highly dependent on combustion temperature, oxygen content and residence time for the reaction to take place (Marques et al., 2007; Omidvarborna et al., 2015c). NOx formation begins after the start of heat release (combustion). Shortly after the end of heat release, the period of NOx formation reduces because temperature of the burned gas decreases (Dieselnet, 2014). Figure 5.3 plots cumulative NOx emissions with time for the engines equipped with EGR and non-EGR, respectively. As shown in Figure 5.3, NOx emissions were much more under control for the EGR engine than that for the non-EGR engine. The non-EGR engine emitted the high amount of NOx at the beginning where it reached 1208 ppm, while the NOx value was 659 ppm for the EGR engine (Table 5.2 and 5.3). After a few seconds the engine equipped with EGR produced NOx with a fairly constant rate, while the rate was still high for the non-EGR engine (7 times higher than EGR engine). In Figure 5.3, it can be observed that the total NOx formation for 1200 seconds for the non-EGR engine is approximately $7 \times 10^5$ ppm, while it is around 105 ppm for the EGR engine.
for 1200 seconds. The lower NOx emissions observed in the EGR engine is because of the fact that the EGR can control the formation of NOx through recirculation of exhaust gas as well as through the regeneration process.

The results clearly indicate that EGR is an effective method for NOx control. NOx emission from EGR engine fueled with B5 was found to be comparatively lower than the NOx emissions from the non-EGR engine. EGR reduces combustion temperature and oxygen content of intake air that are the main factors in NOx reduction (Pradeep and Sharma, 2007; Saleh, 2009). In addition, in idle mode, diesel engines generally tolerate a higher EGR ratio because re-circulating engine exhausts contain high concentration of oxygen and low concentration of carbon dioxide (Agarwal et al., 2011b). The EGR ratio is defined as follows (Agrawal):

\[
\text{EGR ratio} = \frac{\text{volume of EGR}}{\text{total intake into the cylinder}} \times 100
\]

Thus, in idle mode, O\textsubscript{2} is available in sufficient quantity while at high loads O\textsubscript{2} reduces drastically. Therefore, NOx is reduced more at higher loads compared to idle mode. Therefore, the major influence on NOx emissions seems to be due to the change in combustion temperature rather than O\textsubscript{2} availability.
5.5.2 Modeling Results

An ANN model was developed to predict NOx from two different engines based on the experimental data. The number of data patterns required for training the network were chosen in such a way that the network was sufficiently trained enough to produce consistent results, and in the meantime the number of remaining data were enough to test the established model. In addition, some data patterns are set aside for validating the network during the process. 70% of total experimental data was selected for training the neural network, 15% for the network’s validation, and the remaining 15% data was used for testing the performance of the trained network. The input data was fed into the neural network toolbox and model parameters were adjusted to determine the optimum network. Then, the accuracy of the network is presented using R-values and calculating absolute errors through the comparison of the predicted values of NOx emissions with the experimentally measured ones. Initially, the designed network was trained by selecting a minimum number of neurons in the hidden layer. Then the numbers of neurons were
increased until the R-value reached the maximum value, and the results showed better reproducibility (lowest error). The number of neurons in the hidden layer for which the error was minimized was selected as the optimum condition. Of all the networks trained, only one of them satisfied this condition and the simplest network was chosen. A network with one hidden layer and 21 neurons proved to be an optimum ANN for the non-EGR engine (called as 4-21-1). In this notation, four represents the number of input variables and one means the resultant (NOx concentration). The same optimum network was obtained for the EGR engine with 26 neurons in hidden layer (7-26-1). The R-values did not improve or converge beyond 21 and 26 neurons in the hidden layer, and therefore, the networks with these numbers of neurons in the hidden layer would be considered satisfactory.

To make sure the precision of investigation, a regression analysis of outputs and desired targets was performed as shown in Figures 5.4 and 5.5 for the selected engines. The graphs obtained from MATLAB toolbox clearly show how well the variation in the output (predicted values) coincided with the targets (experimental values). If this number is equal to 1, then there is perfect correlation between targets and outputs. Therefore, there is a strong correlation between the predicted values by the ANN model and the measured values resulted from experimental tests. The ANN model for non-EGR engine displayed excellent overall agreement with the experimental data wherein it showed excellent R-values 0.99567, 0.99479, and 0.99668 for training, validation, and testing, respectively. The same trend was observed for the EGR engine as shown in Figure 5.5. The R-values for the same parameters for the EGR engine were 0.99955, 0.99784 and
0.99968. This is corroborated by the consistent concurrency of the ANN predicted values with the experimental data for the entire range of observations.

Figure 5.4. Overall R-values of the developed network for non-EGR engine.
The comparison of ANN predictions for NOx emissions with the experimental data is shown in Figures 5.6 and 5.7 for the non-EGR and EGR engines, respectively. The results confirmed that the ANN modeling with the standard feed forward back-propagation algorithm and LM training algorithm very well represented the experimental data from different idling engines with various input parameters (Najafi et al., 2009; Ghobadian et al., 2009; Kiani et al., 2010; Taghavifar et al., 2014). The major discrepancies were observed at the beginning of the running process where the engines were not stable and the engine load was being increased. It can be observed that the
agreement of the prediction increases slightly in the case of the engine equipped with EGR compared to the non-EGR engine. EGR affected the correlation between the input and output parameters and slightly reduced the error. In other words, EGR is thought to reduce the combustion peak temperature as well as the intake oxygen concentration that resulted in lower emission of NOx. In addition, because EGR can control NOx formation and dampen sudden variations (see Figures 5.6 and 5.7), the pattern of NOx emissions obtained from the EGR engine is less complex and smoother than that of the non-EGR engine and can be predicted by the model with less error.

Figure 5.6. Comparison of experimental and ANN predicted NOx for the non-EGR engine in cold idle mode.
Figure 5.7. Comparison of experimental and ANN predicted NOx for the EGR engine in cold idle mode.

5.6 Conclusion

The present study investigated the applicability of ANN to predict NOx emissions from two in-use engines (non-EGR and EGR engines) operating with B5 fuel in cold idle mode. Methodology and the performance of the NOx ANN modeling were appraised using the R-value as an evaluation criterion. The results showed that three-layer neural network modeling along with the back-propagation feed-forward neural network, combination of logsig transfer functions, and the LM training algorithm predicted NOx emissions in close agreement with the experimental data. R values were very close to one for training, validating, and testing of the network, when 21 (4-21-1) and 26 (7-26-1) neurons in hidden layers were selected for the non-EGR and EGR engines. With the R-values very close to one, the ANN modeling appears to predict the experimental data
with the average R-values of 0.99567 (without EGR) and 0.99954 (with EGR) for tested engines, respectively.

Fuel composition is an important factor that impacts NOx emissions in addition to engine conditions. Biodiesel fuels were obtained from various feedstocks, while soybean is the common type of fatty acid methyl ester (FAME) in US. Methyl esters in biodiesel fuels cover a range of molecules (mainly C12 to C18) including saturated and unsaturated chains, in which their compositions are relatively unique for each feedstock. The degree of unsaturation of biodiesel appears to have a proportional relationship with NOx emissions. Highly unsaturated molecules in biodiesel such as C18:2 (C18:2 represents a methyl ester with 18 carbon atom and 2 double bonds) and C18:3 appeared to cause more NOx emissions. Therefore, biodiesel with saturated chains would help reduce NOx emissions. Thus, double bonds in FAMEs (C18:2 and C18:3) have a significant impact on the formation of NOx, while oleic fatty acid (C18:1) and saturated methyl esters helped NOx formation reduce. Consequently, as long as the biodiesel unsaturation degree is relatively the same as the ones that were used in our ANN model development and the biodiesel fuel blended with the ULSD at 5 vol% used in a bus under similar engine conditions to the ones used in our modeling, the model would simulate NOx emissions from biofuels derived from sources other than soybean within an acceptable range.

The result demonstrated that ANN has potential for predicting engine emissions under idle test. However, appropriate training data and input parameters must be used. With sufficient data and parameters available for input, the use of ANN may be a powerful tool for predicting engine exhaust emissions without conducting complicated, expensive, and time consuming experiments.
Chapter Six

Stochastic Simulation Study

The purpose of this study is to experimentally analyze the NOx emissions from laboratory experiments on a blend of biodiesel fuel with the aid of SSA\(^1\).

6.1 Introduction

Biodiesel is made from vegetable oils and animal fats and it can be used in existing diesel engines with no or minor modifications (Omidvarborna et al., 2014; Kumar et al., 2014). Biodiesel is regarded as environmentally-friendly fuels with low emissions of pollutants such as CO, PAH, sulfur compounds and particulate matter (PM). However, its effects on NOx emissions remain uncertain (Omidvarborna et al., 2015a; Omidvarborna et al., 2015b). NOx emissions are mainly associated with combustion temperature and the physicochemical properties of biodiesel, e.g., the presence of the heterogeneous oxygen atoms in the ester functional group (\(-\text{COO}–\)), compared to the traditional fossil fuels. Therefore, to predict the NOx concentration in the biodiesel exhaust emissions, it is important to understand the effects of combustion temperature and the chemical structure of biodiesel on NOx emissions.

\(^1\) The content of this chapter is submitted for publication entitled as “Prediction of NOx emissions from a simplified biodiesel surrogate by applying stochastic simulation algorithms (SSA)”.

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Regarding the combustion temperature, as the demand for more fuel-efficient vehicles increases, a new strategy known as low-temperature combustion (LTC) gains much attention in auto manufacturers and consumers around the world. LTC reduces the NOx emissions in engines by recirculating some of the exhaust gases, which is proven to be a very effective and practical NOx reduction technique. With LTC, the combustion temperatures are lower thus significantly reducing NOx formation.

Due to the large size and complexity of the combustion reactions associated to fatty acid methyl esters (FAMEs), the main components of biodiesel fuels, the combustion mechanism is extremely complicated, and modeling of it is a very challenging task. Westbrook et al. (2011) developed a detailed mechanism for biodiesel combustion with more than 4,800 species and nearly 20,000 reactions, and, practically it is often replaced with a single and relatively simple species called a surrogate that exhibits similar characteristics to the actual FAMEs. A suggested surrogate should be small enough to be readily investigated with simple calculations while it should be large enough to represent the actual combustion mechanisms and emissions accurately. Accordingly, a few detailed mechanisms (Fisher et al., 2000; Gaièl et al., 2007; Herbinet et al., 2008; Westbrook et al., 2011; Chang et al., 2015) were proposed as the base mechanisms to derive main combustion pathways of simple surrogates with lower computational costs (Fisher et al., 2000; Westbrook et al., 2011). In addition, it is reported that computational run times on a single processor are proportional to the square of the number of species and the squared number of computational grid points (Aceves et al., 2001). Thus, alternative methods with simpler approach are favorable to investigate the combustion mechanisms of large biodiesel molecules. In this study, the SSA is used
with one surrogate to predict NOx emissions. Preliminary information regarding the SSA method is presented below.

6.1.1 Monte Carlo (MC) Simulation
The concept of stochastic approach takes its stand from the fact that collisions in a system of molecules in equilibrium occur in an essentially random manner. In 1976, Gillespie developed the SSA to model networks of reactions via Monte Carlo (MC) methods (Gillespie, 1976 and 1977). The SSA algorithm evolves a system by one reaction at a time, choosing a specific reaction to perform, changing the counts of reactant and product molecules via their stoichiometric coefficients. In doing so, it advances time by an appropriate interval, and updates the probability distribution of future reactions to reflect the outcome of the selected reaction. Furthermore, the type of reaction that occurs in the next step and the time at which it occurs are determined using random numbers and probabilistic rules that ensure accurate sampling. However, the SSA often makes the calculation slow because it simulates every reaction step. In the SSA, a propensity that is computed for each reaction is proportional to its probability of occurrence relative to other reactions (Gillespie, 1976 and 1977; Slepoy et al. 2008). Detailed description of the SSA and application of MC methods to generate model parameters (e.g., time interval) are presented elsewhere (Gillespie, 1976 and 1977; Ahn et al., 2008).

6.1.2 Objectives
The main focus of this study is to apply the SSA on the simplified reaction pathways for NOx emissions from biodiesel at LTC conditions. Therefore, a simplified biodiesel surrogate model based on a previously published biodiesel mechanism (60 species and 172 reactions by Chang et al., (2015)) is used with the components of n-
decane (ND), MD, and methyl-5-decanoate (MD5D), as shown in Figure 6.1. The low complexity of the simplified reaction mechanism enables it to be integrated into the SSA model to simulate the combustion characteristics. The predicted concentration values of combustion byproducts are compared with the concentrations observed in the laboratory experiments that simulated single cycle combustion in a combustion chamber. The experimental conditions included combustion of three different biodiesel fuels at LTC (below 700 K), where the initial pressure and air-fuel ratio (Φ) values were 200 psi and 1, respectively.

![Chemical structures of components of biodiesel surrogate used in this study.](image)

Figure 6.1. Chemical structures of components of biodiesel surrogate used in this study.

### 6.2 Model Development

#### 6.2.1 Biodiesel Surrogate

The surrogate components used in the modeling are methyl esters and normal alkane. Methyl ester is introduced to simulate the oxidation characteristics of ester groups of biodiesel, while normal alkane is employed to compensate the energy content and C/H/O ratio of actual biodiesel. It was found that a surrogate model containing n-alkanes better represented the C/H/O ratio and the energy content of actual biodiesel fuel (Brakora et al., 2009; Ismail et al., 2013). Most previous surrogate models considered only MB as a representative of saturated methyl esters (Dooley et al., 2008; Golovitchev and Yang, 2009; Ismail et al., 2013; Liu et al., 2013; Ng et al., 2013). MB, a C₅ species, is of a manageable size for simulation and it has the similar RC(=O)OCH₃ chemical structure to biodiesel (Brakora et al., 2009).
Only a few reduced mechanisms with long-chain esters are available at present, and almost all the recent mechanisms have been obtained by reducing Herbinet et al.’s (2008) mechanism that consists of n-heptane, MD, and methyl-9-decenoate (MD9D) with 8580 reactions and 3034 species. Due to the recent emergence of new database for various physicochemical properties of biodiesel, different biodiesel surrogates and their reaction pathways have been introduced (Omidvarborna et al., 2015c; Omidvarborna et al., 2016a). However, due to the complicated molecular structure of these components, it is still a significant challenge to develop either a comprehensive combustion mechanism or a well-simplified mechanism for biodiesel fuels.

6.2.2 Skeletal Mechanism

Recent studies highlight that biodiesel surrogate fuels with large molecules represent actual biodiesel fuels better for combustion modeling and simulation (Brakora et al., 2009; Luo et al., 2012a and 2012b). These large surrogate molecules are neither as complex as those of long chain methyl esters nor as small as MB and they are more manageable for combustion calculations compared to larger molecules (Gaïl et al., 2008; Westbrook et al., 2011). Feasibility of these surrogate molecules has been previously validated under a variety of experimental conditions (Chang et al., 2015). While the combustion mechanisms of these surrogates are by no means completely accurate, it is thought that the surrogates are sufficient enough to provide qualitative insight into the reaction pathways in the biodiesel combustion. In the current work, the combustion mechanism modeling and simulation are performed using a surrogate molecule, MD, MD5D, and ND, and the results are analyzed in terms of the mole fraction of NOx in the exhaust emissions.
The most recent combustion mechanism for biodiesel surrogates was obtained by Chang et al. (2015) through merging the large-molecule sub-mechanisms of ND (Chang et al., 2013), MD, MD5D, reduced C2–C3 (Patel et al., 2004) and H2/CO/C1 (Klippenstein et al., 2011) as shown in Figure 6.2. Figure 6.2 demonstrates the main reaction pathways for the main components of the biodiesel surrogate. The R11-R20, R21-R28, R31-R38, and R41-R46 reactions represent the simplified pathways for ND, MD, MD5D, and MP2D (ester group) reactions, respectively. A decoupling methodology was used to depict the oxidation of the small molecules (e.g., H2/CO/C1), while a simplified mechanism (Chang et al., 2013) was used for C2–Cn species (n is the number of carbon atoms in the fuel molecule). Due to the size of the simplified mechanism, Chang et al.’s model significantly reduced the number of species involved in the combustion, where no isomers for large molecule radicals were considered (Chang et al., 2015). Although the SSA remains as a computationally demanding approach which limits its applicability, especially for large reaction networks required for modeling more realistic networks, the size of the simplified mechanism can be well controlled by the SSA. The SSA takes time steps of variable length, based on the rate constants and population size of each chemical species (Burrage et al., 2004).
According to the literature (Metropolis et al., 1953; Gillespie, 1976), MD and MD5D mainly produce alkylester radicals through H-abstraction reactions ($R_{21}$ and $R_{31}$) as shown in Figure 6.3. This reaction happens via H-abstraction through the carbon atom in the ester group, which results in MDJ formation from MD. MDJ, MD5DJ and MP2D. The H-abstraction reaction generates intermediate oxygenated species that lead to lighter HCs such as $C_6H_{13}CHO$, $C_8H_{11}CHO$, $C_2H_3CO$ and methoxycarbonyl ($CH_3OCO$) through the radical reactions as presented in Figure 6.3. Light HCs form $CH_3O$ and $CH_2CO$, and $CH_3O$ that become methyl aldehyde ($CH_2O$), then CHO, and finally CO and CO$_2$. $CH_3OCO$ is an important intermediate product in biodiesel combustion (Lapuerta et al., 2008), because it finally produces CO$_2$ (Gaïl et al., 2007; Dooley et al., 2008), which is a
unique characteristic of methyl esters (Herbinet et al., 2008; Diévart et al., 2012). Therefore, if a biodiesel surrogate has a short chain length, it may form more oxygenated products such as CO, CO₂, CH₄ and CH₂O, and less carbon atoms are left to form unsaturated HCs such as ethane and acetylene which are thought to be PAHs precursors (Gaïl et al., 2007; Dooley et al., 2008). Moreover, in Figures 6.2 and 6.3, it can be seen that the two oxygen atoms of the ester group finally lead to CO₂ formation in the pathways of ester group reaction. It means that two oxygen atoms of ester group capture the carbon atoms from a pool of carbon atoms that may form PAHs precursors otherwise (Omidvarborna et al., 2016a). This oxygen reaction of ester group with carbon could be the reason for the higher CO₂ formation in biodiesel combustion than in regular diesel. The main molecular reaction mechanisms for MD and MP2D are illustrated briefly in Figure 6.3.
Figure 6.3. Detailed chemical pathway of major species in MD sub-mechanisms with their structures.

A relatively detailed MP2D mechanism is included because the MP2D-related reactions are the major ester group reactions, which are important for the oxidation of methyl esters (Diévart et al., 2012). The light HCs such as C$_3$H$_6$, C$_2$H$_4$, and C$_2$H$_2$ species are also included as they can potentially contribute to NOx formation. Finally, a reduced NOx sub-mechanism (Brakora et al., 2009; Yoshikawa and Reitz, 2009) is added to investigate NOx emission formation as tabulated in Table 6.1.

As shown in Figure 6.4, of the various NOx formation mechanisms, $\text{CH} + \text{N}_2 \leftrightarrow \text{HCN} + \text{N}$ reaction, is one of the important reactions with a lower activation energy than thermal NOx reactions (Liberman, 2010). As stated above, the oxygen atoms bound to

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one carbon atom in the methyl ester moiety lead to the increase of CO/CO$_2$ formation. In addition, the double bond in methyl ester leads to a high combustion temperature (Szybist et al., 2005), and possibly to the increase of thermal NOx formation (Shu et al., 2013). Therefore, in the modeling study, the role of methyl ester moiety in the increase of NOx formation is very important, and is included in the combustion mechanism accordingly.

The main Arrhenius rate constants used in the simplified mechanisms are also summarized in Table 6.1. The ND, MD, and MD5D sub-mechanisms are described in detail in (Fisher et al., 2000), and (Ng et al., 2013). Optimization of reaction rate constants for the biodiesel surrogate can be found elsewhere (Chang et al., 2013; Chang et al., 2015).

Table 6.1. The main reaction kinetics used in this study ($k = A \cdot T^n \cdot e^{(-E/RT)}$). The units of $A$ are cm$^3$/mol/s, $T$ is in K, and $E$ is in cal/mol (Metcalfe et al., 2007; Yoshikawa and Reitz, 2009; Chang et al., 2013; Chang et al., 2015).

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Arrhenius rate constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$A$</td>
</tr>
<tr>
<td>R11</td>
<td>$C_{10}H_{22} + O_2 = C_{10}H_{21} + HO_2$</td>
<td>2.00E+15</td>
</tr>
<tr>
<td>R12</td>
<td>$C_{10}H_{21} + O_2 = C_{10}H_{20} + HO_2$</td>
<td>3.16E+11</td>
</tr>
<tr>
<td>R13</td>
<td>$C_{10}H_{21} = 2C_3H_6 + C_2H_2 + C_2H_4$</td>
<td>4.00E+13</td>
</tr>
<tr>
<td>R14</td>
<td>$C_{10}H_{21} + O_2 = C_{10}H_{21}OO$</td>
<td>2.00E+11</td>
</tr>
<tr>
<td>R15</td>
<td>$C_{10}H_{21}OO = C_{10}H_2OOH$</td>
<td>5.51E+13</td>
</tr>
<tr>
<td>R16</td>
<td>$OOC_{10}H_2OOH = C_{10}ket + OH$</td>
<td>8.91E+10</td>
</tr>
<tr>
<td>R17</td>
<td>$C_{10}ket = CH_2O + C_6H_{11}CO + OH + C_3H_6$</td>
<td>1.98E+16</td>
</tr>
<tr>
<td>R18</td>
<td>$C_3H_1CO + O_2 = C_3H_2 + C_3H_3 + CO + HO_2$</td>
<td>3.16E+13</td>
</tr>
<tr>
<td>R19</td>
<td>$C_3H_3 + O_2 = 2C_3H_6 + C_2H_5 + C_2H_4 + HO_2$</td>
<td>3.16E+13</td>
</tr>
<tr>
<td>R20</td>
<td>$C_{10}H_{20} + O_2 = 2C_3H_6 + C_2H_5 + CH_2O + HCO$</td>
<td>3.16E+13</td>
</tr>
<tr>
<td>R21</td>
<td>$MD + O_2 = MDJ + HO_2$</td>
<td>3.00E+14</td>
</tr>
<tr>
<td>R22</td>
<td>$MDJ = C_3H_7 + 2C_2H_4 + MP2D$</td>
<td>8.00E+13</td>
</tr>
<tr>
<td>R23</td>
<td>$MDJ + O_2 = MDJO_2$</td>
<td>2.00E+11</td>
</tr>
<tr>
<td>R24</td>
<td>$MDJO_2 = MDOOH$</td>
<td>5.51E+13</td>
</tr>
<tr>
<td>R25</td>
<td>$MDOOH + O_2 = O_2MDOOH$</td>
<td>2.00E+11</td>
</tr>
<tr>
<td>R26</td>
<td>$O_2MDOOH = MDket + OH$</td>
<td>8.91E+10</td>
</tr>
<tr>
<td>R27</td>
<td>$MDket = C_6H_{11}CHO + CH_2CO + CH_2OCO + OH$</td>
<td>1.98E+15</td>
</tr>
<tr>
<td>R28</td>
<td>$C_6H_{11}CHO + O_2 = C_6H_7 + C_3H_6 + CO + HO_2$</td>
<td>3.16E+13</td>
</tr>
<tr>
<td>R31</td>
<td>$MD5D + O_2 = MD5DJ + HO_2$</td>
<td>6.00E+14</td>
</tr>
<tr>
<td>R32</td>
<td>$MD5DJ = C_3H_4 + 2C_2H_4 + MP2D$</td>
<td>8.00E+12</td>
</tr>
<tr>
<td>R33</td>
<td>$MD5DJ + O_2 = MD5DJO_2$</td>
<td>2.00E+11</td>
</tr>
</tbody>
</table>
6.3 Modeling Validation

To evaluate the performance of the SSA model, the simplified ND/MD/MD5D mechanism is used to simulate NOx emissions. Experimental data that have been collected from combustion of selected pure biodiesel fuels with different range of unsaturation (46.2 - 85.1%) are used for comparison (Omidvarborna et al., 2015c). Among the tested biodiesel fuels, SME is the most unsaturated, WCO medium unsaturated, and TO was the least unsaturated (Omidvarborna et al., 2015c). SME has the longest chain length, and WCO and TO are the relatively short chain length fatty acids (Omidvarborna et al., 2015c). The simulation was performed using the SSA at the temperature range below 700 K that was also used in the experiments. Since NOx formation is related to high oxygen concentration, the air-fuel ratio was set as 1.0, the same condition used in the experiments (Shu et al., 2013).

Figure 6.4(a) shows the SSA modeling result (blue line) and experimental results (triangular marks) for pure biodiesel fuels ranging from highly-unsaturated (SME in red),

| R34 | MD5DJO₂ = MD5DOOHJ | 5.51E+13 | 0.00 | 19,000 |
| R35 | MD5DOOHJ + O₂ = O₂MD5DOOH | 2.00E+11 | 0.00 | 0 |
| R36 | O₂MD5DOOH = MD5Dket + OH | 8.91E+10 | 0.00 | 17,000 |
| R37 | MD5Dket = C₆H₁₁CHO + CH₃OCO + CH₃CO + OH | 8.98E+15 | 0.00 | 43,000 |
| R38 | C₆H₁₁CHO + O₂ = C₁₃H₂₅ + C₁₃H₆ + CO + HO₂ | 3.16E+13 | 0.00 | 10,000 |
| R41 | MP2D + OH = MP2DMJ + H₂O | 7.02E+07 | 1.60 | -35 |
| R42 | MP2D + H = MP3J | 1.00E+13 | 0.00 | 2,900 |
| R43 | MP2DMJ = C₆H₇CO + CH₃O | 5.75E+23 | -2.80 | 23,540 |
| R44 | MP3J = C₁₃H₂₅ + CH₃OCO | 2.91E+13 | 0.17 | 33,670 |
| R45 | C₂H₂CO + M = C₂H₃ + CO + M H₂O/16.25/ CO/O/1.875/ CO₂/3.75/ CH₄/16.25/ | 8.60E+15 | 0.00 | 23,000 |
| R46 | CH₃OCO = CH₃ + CO₂ | 7.98E+12 | 0.33 | 15,640 |
| N1 | CH₃ + N₂ = HCN + N | 3.12E+09 | 0.90 | 20,130 |
| N2 | N + O₂ = NO + O | 9.00E+09 | 1.00 | 6,500 |
| N3 | N + OH = NO + H | 3.36E+13 | 0.00 | 385 |
| N4 | HO₂ + NO = NO₂ + OH | 2.11E+12 | 0.00 | -480 |
| N5 | HCN + OH = NH₂ + CO | 5.96E+05 | 3.20 | 8,210 |
| N6 | NH₂ + O = H₂ + NO | 3.90E+13 | 0.00 | 0 |
relatively medium-unsaturated (WCO in purple) and low-unsaturated (TO in green) fuels. The mole fraction of NOx in the exhaust is plotted in terms of the peak combustion temperature, where it is affected by FAME’s composition for each feedstock. The NOx concentrations calculated in the simulation follow the similar trend as the experimental data.

Figure 6.4(b) shows the prediction of the SSA model when the biodiesel fuels blended with ultra-low sulfur diesel (ULSD) in proportions of B20 (20% biodiesel, 80% ULSD) and B50 (50% biodiesel, 50% ULSD). The results are plotted with their standard deviations for the both NOx mole fraction in terms of the peak combustion temperature (X-axis). As the content of ULSD increases in the blends, the peak combustion temperature increases (Omidvarborna et al., 2015c). This temperature increase may result in the formation of thermal NOx. The SSA model predicts well the mole fraction of NOx from B50, B20, and ultra-low sulfur diesel (ULSD) fuels, which mean that the ND mechanisms are well suited in the simulation. Although the NOx values are overestimated, the agreement between the SSA model and experimental results are reasonable. It is thought that the differences in the C/H/O ratio and ester group concentration between the surrogate model and real biodiesel fuels may be responsible for the discrepancies.
Figure 6.4. Comparison of experimental (symbols) data points and predicted (lines) NOx concentrations in a laboratory combustion reactor under LTC conditions at Φ = 1.0 and initial pressure of 200 psi (13.8 bar), (a) SSA comparison with pure biodiesel fuels only, (b) SSA prediction with average values.
The experimental values of pure biodiesel fuels (Omidvarborna et al., 2015c) versus the predicted values from the SSA are plotted along the diagonal line as shown in Figure 6.5. The diagonal lines represent the equality between the experimental and simulation values. The data points located close to the line indicate agreement of the simulation results with the experimental results. Nearly all the experimental data are located within the scatter bands of +20% for SME and WCO fuels. The results for TO are greater than +20%, meaning the model over-predicted the NOx emissions. MD and MD5D have shorter chain lengths than methyl esters in biodiesel fuels (C_{12}-C_{18}), which is thought that the selected surrogate provides extra oxygen for combustion (because of short chain length and high oxygen-to-carbon ratio) than the experimental results. Therefore, biodiesel surrogate should have a higher peak combustion temperature and possibly emits more NOx emission than the experimental data. In addition, the SSA shows better prediction of NOx concentrations for the biodiesel with unsaturated fatty acids than the ones with saturated fatty acids. It is suggested that the reaction pathways be expanded to include possible side reactions, especially for MD and MD5D, to reduce the deviations. However, it will make the model more complex. For the current model, the root mean square error (RMSE) values confirm the dependence of the degree of unsaturation on better agreement of the SSA model with the experimental values. The RMSE values for SME (highly unsaturated), WCO, and TO (saturated) are 0.0020, 0.0019, and 0.0029, respectively. The RMSE values show that the overall agreement between the experimental data and the predictions from the biodiesel surrogate (ND/MD/MD5D) is considered satisfactory.
Figure 6.5. Measured values vs. predicted values by SSA for pure biodiesel fuels (SME, WCO, and TO).

6.4 Conclusion

Understanding of the oxidation mechanism and kinetics of MB will significantly contribute to the development of reliable kinetic models for methyl esters and consequently real biodiesel fuels. Thus, the need for larger methyl esters, including both saturated and unsaturated in practical biodiesel is imperative. In this study, a simplified chemical reaction mechanism for combustion of biodiesel fuels is simulated using the SSA and Monte Carlo simulation. The results are validated against the experimental data for the mole fraction of NOx in the exhaust emissions. Biodiesel surrogates, MD and MD5D, are used as representatives of saturated and unsaturated methyl ester, and ND is included to match the energy content of the surrogates with ULSD. The SSA can be a simple and feasible algorithm for simplified surrogates to predict the combustion byproducts of biodiesel with relatively good agreement. By varying the ratios of
surrogates, it is possible to simulate the combustion of different types of biodiesel that have different compositions of saturated and unsaturated fatty acids. The overall agreement between the SSA predictions and experimental data is satisfactory, but the current model underestimates NOx concentration for TO by more than 20% compared to SME and WCO that have more unsaturated fatty acids than TO. It is thought that the difference between chemical characteristics of the surrogate and real FAMEs has a major impact in this deviation. In addition, more detailed analysis and comparison of biodiesel surrogates are required to improve the prediction through SSA simulation. Moreover, a careful selection of side reactions and inclusion of them in the combustion mechanisms would increase the model performance.
Chapter Seven

Conclusions and Recommendation for Future Work

7.1 Conclusions

The dissertation summarizes the study results that will provide a basis for consideration of strategies to deal with the methodology for the analysis of combustion chemistry of biodiesel for the use in urban transit buses, in both laboratory and field study. This study attempts to assess the opportunities and obstacles inherent in the methodology. By presenting a methodology, the results of this study specifically address the lack of published data on combustion chemistry of three common biodiesel fuels and their characteristics on NOx, carbon, and soot emissions. Different characterization techniques as well as modeling studies were used for evaluating the environmental and health impacts of carbonaceous particles produced by biodiesel combustion.

Modeling of soot formation has to address many aspects of ULSD and biodiesel combustion. From the literature review, to develop a robust and reliable model for soot combustion, it was determined that more reasonable assumptions need to be made based on chemical and physical characteristics of the fuels. In addition, it was observed that a fundamental challenge in soot particle study for alternative fuels is the inability to predict
differences in soot formation for different feedstocks and their blends with regular diesel. Therefore, further research needs to be carried out to understand the relationship of fuel’ characteristics (especially unsaturation content and chain length) on characteristics of soot emissions.

A lot of studies have been done to investigate the effect of the biodiesel and its blends on exhaust emissions as compared to diesel. Reduction of soot and HCs emissions by using biodiesel fuels may help reduce the deleterious impact of global warming and climate change. However, formation of NOx from combustion of biodiesel fuels were reported to increase. Moreover, CO and CO$_2$ emissions from combustion of different biodiesel fuels vary according to the type of chemical characteristics of source materials. Therefore, the emissions of NOx, CO and CO$_2$ were measured to investigate the input of biodiesel fuels’ structures.

The difference in NOx emissions between the neat biodiesel samples and ULSD was obtained. The degree of unsaturation of biodiesel appeared to have a proportional relationship with NOx emissions (e.g., SME produced more NOx emissions than TO and WCO). Highly unsaturated molecules (C18:2 and C18:3) appeared to cause more NOx emissions. However, biodiesel with saturated chains would help reduce NOx emissions. The paired t-test results confirmed that there were significant differences in NOx emissions between the neat biodiesel samples and ULSD.

The results of soot characterization study showed that the unsaturation of biodiesel fuel was correlated with soot characteristics. The addition of biodiesel in blends reduces the inception of soot precursors and it reduces the size and number of soot particles through further oxidation with extra oxygen included in biodiesel. Eight
elements (Al, Ca, Cu, Fe, Mg, Mo, Na, and P) were detected as the marker metals in biodiesel soot particles. Biodiesel soot oxidized faster than ULSD soot, and this rate is related to fuels’ properties (e.g., unsaturation degree, chain length).

The results of carbon analysis confirmed that the variation in the properties of the biodiesel led to the different carbon emissions over a range of combustion conditions. As the unsaturation degree increased, chain length increased and vice versa, therefore, the degree of unsaturation and chain length of FAMEs in biodiesel fuels are related and they are thought to be the causes for the results observed. Short FAMEs such as WCO emit more CO\(_2\) than long ones like SME. CO emission is higher with increasing chain length and unsaturation of FAMEs. The more is biodiesel unsaturated, the higher it may produce CH\(_4\) emissions.

In the field study, the results of the PM emission analysis showed the dependency of collecting PM on engine model, idle modes (cold and hot), and fuel type. The number of heavy metals in PM emitted during hot idling was greater than those from cold idling. It was observed that Ca was the most-abundant element in cold idle mode (76% and 82% of average total mass for the 700 and 800 series, respectively). While, for the hot idle test, the dominant elements were observed Na and Ca with 71% and 72% in mass for the 700 and 800 series, respectively. It can be seen that the collected samples from the tail pipe emissions contained significantly more Ca than the other elements. Therefore, Ca is reported as a typical marker for exhaust emissions in various engine types. The carbon speciation of PM from transit buses in idle mode (both cold and hot) was evaluated and the results indicated that the use of biodiesel could effectively reduce EC (by 10%) and increase the portion of OC emission (by 90%) in some cases. Between the idling modes,
hot idling appeared to produce more EC than cold idling, and therefore it should be avoided.

ANN has potential for predicting engine emissions under idle test. However, appropriate training data and input parameters must be used. The results showed that three-layer neural network modeling along with the back-propagation feed-forward neural network, combination of logsig transfer functions, and the LM training algorithm predicted NOx emissions in close agreement with the average R-values of 0.99567 (without EGR) and 0.99954 (with EGR) for tested engines, respectively. RMSE values were in the acceptable range for non-EGR and EGR engine series, respectively. Thus, EGR proved to be a useful tool to control NOx emissions from idling engines. Therefore, the use of ANN can be a powerful and simple tool for predicting emissions without conducting complicated, expensive, and time consuming experiments.

Additionally, modeling of the exhaust emissions by using simplified reaction kinetics and skeletal mechanism with stochastic approach was acceptable. SSA approach was implemented to predict NOx species in the exhaust, where the combustion mechanism for the biodiesel surrogate was constructed from a biodiesel surrogate. Biodiesel surrogates, MD and MD5D, are used as representatives of saturated and unsaturated methyl ester, and ND is included to match the energy content of the surrogates with ULSD. The overall agreement between the SSA predictions and experimental data is satisfactory, but the current model underestimates NOx concentration for TO by more than 20% compared to the SME and WCO that have more unsaturated fatty acids than TO. It is thought that the difference in C/H/O ratio and ester group concentration between the surrogate model and real biodiesel fuel might be
responsible for this deviation. Considering semi-detailed NOx formation mechanisms may result in a better prediction on NOx emission, however, it will make the model more complex. In addition, more detailed analysis and comparison of biodiesel surrogates are required to improve the prediction through SSA simulation.

The results presented here provide additional justification for the use of biodiesel as an alternative fuel along with other engine technologies and modifications, because, in addition to providing a renewable energy source to the transportation sector and reducing exhaust emissions, biodiesel may provide another advantage in the reduction of GHG emissions.

7.2 Recommendation for Future Work

The following recommendations are an outcome of the knowledge gained in the course of conducting the present research. The identified objectives may improve and add further to the knowledge base and fill in the information gaps currently in the field of combustion chemistry of biodiesel fuels for the use in transit vehicles. From the present study, the following suggestions can be drawn:

7.2.1 PM Characterization and Emission Control

Current research on real engines has focused on several challenges. Those challenges include 1) improving the performance and emissions of engines running on the binary (diesel–biodiesel) and ternary (ethanol–biodiesel–diesel) blends, 2) developing surrogates and their combustion models via commercial software programs, 3) finding new feedstocks for biodiesel production, and applying oxidants and additives to improve combustion and emissions. In addition, characterization, size measurement and emission control of PM are still under consideration by many research centers (He et al., 2016;
Mofijur et al., 2016; Ramadhas and Xu, 2016), because of their importance for regulatory agencies. Although reducing the size of soot particles and aggregates may seem to be the solution to the number of problems that PM causes, decreasing the size below a certain level, e.g., less than PM_{10} or PM_{2.5}, will have adverse health effects. Therefore, characterization and PM size measurement from engine exhaust during different operation modes may lead to precisely classify particles and determining the variables affecting PM specifications (Omidvarborna et al., 2014; Shirmohammadi et al., 2016).

The current study suggests that EGR technology significantly reduces the mass of PM and emission of NOx. However, study on PM emissions and exhaust gases of other biodiesel blends (B5, B10, B20, B50 and B100) of available feedstocks from all over the world on at least one set of the public buses (two buses, EGR and non-EGR engine) will be an important stage of research in the future. This is because of the fact that fine and ultrafine particles of PMs, which are emitted from combustion of fuels, have higher specific surface areas and toxic effects than coarse particles in addition to the carcinogenic species directly from an engine itself. Therefore, understanding the specification of PMs from new feedstocks is still considered significant. In addition, the results of engine exhausts particle sizer (EEPS) spectrometer and/or scanning mobility particle sizer (SMPS) for real-time particle size distribution measurements should be tested in future experiments. The obtained PM size distribution can be compared both with the literature data and the selected laboratory experiments. Another technique which is highly recommended for field studies is a particle counter instrument, which can be used to detect and measure the real-time number concentration (particles/cm^3) of particles. A comprehensive PM analysis from real engines by using these instruments
will improve our knowledge and strengthen the database. It will also help regulatory agencies with their decision making process for standards and regulations on tail pipe emissions in future.

Although the results of the current study cover PM characterization, other gaseous emissions for emerging biodiesel feedstocks and blends should be considered on real engines to better understand the effects of engine factors (e.g., engine parts, engine load, EGR, etc.) on emissions in comparison to ULSD and SME fuels (Can et al., 2016). Although, the effects of the fuel’s characteristics on the selected emissions have been studied, more in-depth field engine experiments should be done to draw a solid conclusion for the new feedstocks. Detailed analysis will confirm which biodiesel feedstock has better performance and lower emissions than the others.

7.2.2 Environmental Data Analysis of Transit Buses

Optimizing the operational efficiencies of public and business transportation systems must be accompanied by the effort to reduce the environmental impacts. The current study is part of a long term study on public transport buses in the city of Toledo, and the data collected in the past years are needed to be classified for their specific categories (e.g., idling and running mode of each bus series). After doing further analysis and statistical adjustments (e.g., normalization), ANN can be implemented to develop a general realistic model and to predict emissions during different modes of operation for a wide range of transport buses (running on ULSD, SMEB5 and SMEB20 fuels). The proposed models will be closely monitored for the surrounding air and related impacts of public transport buses on human health in urban areas. This is because of the fact that policy makers need to know how important the problem is relative to other social
concerns and how to prevent or adapt to air pollution in ways that minimize costs to society.

7.2.3 Combustion Chemistry and Proposing a Synthetic Biodiesel Fuel

Current discussions emphasize the processes to make various biodiesel fuels and fuel additives, the compatibility of these substances with current fuel-delivery infrastructure and engine performance, and the competition between biofuel and food production. However, the combustion chemistry of the biodiesel fuels, has not received much attention. Biodiesel fuels are oxygenated fuels, containing oxygen as an additional element in their molecular constitution. This feature distinguishes them from the HCs in conventional petroleum-based fuels, the combustion chemistry of which has long been studied. The presence of oxygen atoms in the oxygenated fuel molecules alters the electronic structure, and almost all the C-H bond strengths for the oxygenated fuels are different from their values for structurally related, more familiar HC fuels (Kohse-Höinghaus et al., 2010). To understand the associated combustion reactions and to identify recurring reaction pathways, it is important to study combustion chemistry of potential biofuels. In this regard, examining the fuel decomposition and oxidation reactions of smaller esters is a valuable step towards understanding the reaction pathways of the large ester molecules found in true biodiesel fuels.

From the combustion perspective, the chemical decomposition and oxidation pathways of current and future biofuels are intimately coupled to the structure of the respective fuel molecule. Predicting the combustion behavior of these fuels, including ignition, extinction, heat release, and the formation of potential pollutants (soot, NOx, etc.), requires the development of detailed combustion mechanisms. Combustion models which are validated with reliable experiments are used to examine all important aspects
of the combustion performance and to transfer the results from the laboratory to the industrial process. While decades of research have been performed to provide such chemical databases for the conventional hydrocarbon fuels, the experience with the richer chemistry of oxygenated fuels is comparatively recent. The combination of chemical functional groups in a FAME molecule may yield reaction sequences not encountered in fossil-fuel chemistry. Therefore, important information to anticipate a biodiesel fuel’s combustion properties, including pollutant formation, may thus be lacking. Such information is urgently required to assist the evaluation of their suitability as replacement fuels.

Research on the different feedstocks from all over the world and their influence on emissions are increasing progressively. The chemical composition of the raw materials used to produce biodiesel is variable, thus providing a wide range of types of biodiesel showing diverse affinity to diesel engines. Moreover, depending on the fuel properties, exhaust emissions may be affected. For these reasons, it is important to increase the knowledge about the implications of biodiesel chemical composition and properties over various conditions in the laboratory combustion chamber. For laboratory study, it is recommended to investigate the effects of pure FAMEs’ characteristics on combustion and emissions. The suggested parameters that should be considered are as follows:

- The effect of selected FAMEs’ chain lengths (C8:0, C10:0, C12:0, C14:0, C16:0, C18:0, C20:0, and C22:0) on combustion and emissions.
- The effect of selected FAMEs’ unsaturation degree (C18:0, C18:1, C18:2, and C18:3) on combustion and emissions.
By running experiments on pure FAMEs, the role of fuels’ specifications (unsaturation, chain length, oxygen content, etc.) on the selected emissions can be examined and compared with other fuels, separately. After conducting a comprehensive study on pure FAMEs and drawing a conclusion on their emissions, a blended fuel, which composes from the pure FAMEs with the lowest emissions and the optimum combustion properties, can be produced. Other physical and chemical specifications (cloud point, caloric value, etc.) of the blended fuel can be measured and compared with the available data. In addition, there might be a possibility to transesterify one of the available raw oils into a biodiesel with similar composition and properties as the blended fuel. Therefore, this fuel (or a real biodiesel fuel with closely similar composition) can be proposed as the biodiesel fuel which is being pursued. In addition, after collecting the emission data from each FAMEs in pure form, SSA can be implemented with higher resolution.

7.2.4 Soot Oxidation Mechanisms

Detailed characterization of biodiesel soot oxidation is very interesting and can reveal some information about the active soot oxidation mechanism. Although current research studies examined the structure of biodiesel soot compared to regular diesel for various conditions (Neoh et al., 2007; Guo et al., 2016; Kholghy et al., 2016; Omidvarborna et al., 2016a), however, the biodiesel soot oxidation mechanism is very complex and further investigation is required on the role of each oxidizer on morphology of soot particles (Guo et al., 2016). It has been discussed that soot oxidation in biodiesel combustion happens via oxygen molecules, but in reality it happens by O radicals and OH species as well (Omidvarborna et al., 2015b). Although the reactivity and diffusivity of these three species are completely different, their effects on the morphology of soot particles in the oxidizing region are not similar (Neoh et al., 2007). While the OH radical
usually acts on the surface and oxidizes the surface of the particles, the O radical can penetrate deep into the soot particles and react with the carbon molecules inside the particles which eventually make them less dense and more porous. As a result, the O radical oxidation breaks down the aggregates and shrinks down the size and diameter of primary soot particles at the same time. But OH oxidation only decreases the size of the soot primary particles and does not affect the overall structure of soot aggregates as much as the O radical. This theory is affected by many other factors such as species concentrations and time available for oxidation and needs further investigation on biodiesel soot characterization. Therefore, for future studies, understanding the exact role of each oxidizer and its effects on emissions (as well as investigating the impacts of its concentration and residence time) will be highly important for scientists and researchers to come up with valid reaction pathways and to be able to control reaction mechanisms to reduce health hazards and to develop biodiesel surrogates.

To sum up, expanding the study to other mobile sources such as garbage trucks, school buses, power generators, airplanes, etc. is recommended as a part of future study. So, it seems reasonable to presume that the use of biodiesel fuels will still keep growing in the near future. However, competition for feedstock supply, development of new engine technologies and concerns about biodiesel degradability and long-term effects on engines has also to be taken into consideration.

7.3 Publications and Presentations

Submitted Papers:


**Accepted and Published Papers & Reports:**

ANN of NOx emission from EGR and non-EGR transit buses in cold and hot idling modes, H Omidvarborna, A Kumar, DS Kim. *Environmental Progress & Sustainable Energy* (In press).


**Conference Proceeding and Publications:**


Application of stochastic simulation algorithms (SSA) to NOx emissions from combustion of simplified biodiesel surrogate fuel in low-temperature combustion (LTC).


**Presentations:**


Kumar, A., Kim, D.S., and Omidvarborna, H., Characterization of Exhaust Particulate Matter from Transit Buses in Toledo, Ohio, Environmental Seminar, Dept. of Civil Engineering, Aligarh Muslim University, January 24, 2013.

Omidvarbona, H., Kumar, A., Kim, D.S., Characterization of Exhaust Emissions From Transit Buses (Brief Review), Air Pollution Course (CIVE 3620) Presentation, The University of Toledo, Toledo, OH, January 28, 2013.
References


size characteristics of emissions from a diesel engine, Environmental Science & Technology 32, 1183–1191.


Shu, G., Xu, B., Zhang, W., Zhao, W., Wei, H., and Zhu, T. (2013). Chemical kinetic modeling for the effects of methyl ester moiety in biodiesel on PAHs and NOx formation, Transactions of Tianjin University 19, 168-173.


