A Thesis

Entitled

Laboratory Experiments on the Emissions from Different Biodiesel Blends in Comparison to B20 and Ultra Low Sulfur Diesel

by

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Biodiesel has been a promising clean alternative fuel to fossil fuels, which reduces the emissions that are released by fossil fuels and possibly reduces the energy crisis caused by the exhaustion of petroleum resources in the near future. Biodiesel is replacing diesel as an alternative fuel for internal combustion engines. Previous research studies have shown that biodiesel greatly reduces carbon monoxide (CO), hydrocarbon (HC) and particulate matter (PM) emissions compared to diesel fuels. At present, B20 (20% biodiesel in the total fuel mix) is being used commonly due to its material compatibility to changing weather conditions, emission benefits and costs. In this study biodiesel blends B5, B10 and B50 were combusted to investigate how the engine conditions influence the emission concentrations of H₂, CO, CH₄, CO₂, N₂ and morphological data of particulate matter. Different emission samples were collected for a certain range of temperatures and pressures. The samples were analyzed using Gas Chromatography and the particulate matter was analyzed using Scanning Electron Microscope images. The samples of different biodiesel blends were then compared with the emissions from B20...
and Ultra Low Sulfur Diesel at the same temperature and pressure ranges. From the results under varied tested conditions it has been inferred that, for low H₂ emissions, B5 combustion under low temperatures and high pressures is preferred. For low CO emissions, B20 combustion under high temperatures and pressures is preferred. For low N₂ emissions, B5 combustion under low temperatures and high pressures is preferred. For low CH₄ emissions, B5 combustion under low temperatures and high pressures is preferred. For low CO₂ emissions, ULSD combustion under low temperatures and low pressures is preferred. H₂ emissions have decreased as the biodiesel blend increased. CO was observed to increase with the blend. The emissions were comparatively lower under low temperatures. N₂ showed an increasing trend with the blend. Low temperatures and high pressure reduced the emissions. Not much variation was observed for CH₄ for the blends under the tested conditions. The CO₂ emission from the results was observed to be on an increasing trend except for B20. Under higher pressures and temperatures CO₂ emissions were lower for all the blends except for B20. ULSD showed lower emissions under low temperatures and varying pressures compared to biodiesel. B5 showed lower emissions under lower temperatures and higher pressures. B10 showed the least emissions under lower temperatures and lower pressures. B20 showed lower emissions under high pressures and varying temperatures. B50 showed the least emissions under lower temperatures and higher pressures except for CO₂ which showed lower emissions under higher temperatures and pressures.
This thesis is dedicated to my father Satyanarayana Penumalla, Mother Sriranganayakamma Karanki, Brother Venkata Srikanth Penumalla, Sister-in-law Dharani Koppisetty, and Mownika Choudhary Bobba.
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Chapter 1

Introduction

1.1 Diesel Engine Exhaust Emissions

Diesel utilizes about two-thirds of the fuel of a similar ignition-based gasoline engine for the equivalent power output. As a result, annual fuel costs for diesels are approximately one-third less than equivalent gasoline power engines. Despite the fuel economy of the diesel and low carbon dioxide emissions, diesel is more harmful to human health on a per-vehicle basis than emissions from similar gasoline-powered engines.

Mobile emissions from diesel engines are considered a direct harmful agent to human health because mobile sources are generally ground-level pollutant sources. Since 1950 there has been a 10% increase in the number of cars every decade due to the rapid increase in population. This increase in the number of vehicles has made the transportation sector a leading contributor to air pollution along with the consumption of fossil fuels, which are non-renewable. Total world consumption of marketed energy is expected to increase by 50% from 2005-2030. As estimated by the Energy Information
Administration’s (EIA) International Energy Outlook (2008), the world demand for crude oil will grow from 87-million barrels/day in 2008 (OPEC estimation) to 103-million-barrels/day in 2015 to over 119-million barrels/day in 2025.

Global ‘‘dieselization’’ occurred rapidly during the last decade, which in turn, caused an uneven fuel production. Due to the growth in rapid consumption of energy, stringent rules were developed for regulating transportation fuels like EN-590 in Europe (UNE EN-590, 2004) and ASTM D 975-06 in the United States (ASTM International, 2006). However, diesel also had very high impacts on human health. According to the U.S. Environmental Protection Agency’s (EPA), National-Scale Air Toxics Assessment (1999), mobile sources are responsible for about 44% of outdoor toxic emissions, almost 50% of cancer risk, and 74% of non-cancer risk health problems. In the U.S., diesel fuel is used in approximately 90% of the transit buses and most of these transit buses, with conventional diesel engines, run in over-populated and polluted areas. This has caused a concern to the EPA which laid out strict emission standards. To meet these standards several states and private vehicle authorities have been operating and experimenting with alternative fuels such as ethanol, ultra-low sulfur diesel (15 ppm sulfur), and different blends of biodiesel. Biodiesel compared to diesel provides better fuel efficiency, torque and horsepower (Bunger et al., 1998, 2000).

The use of biodiesel is not a new concept. Rudolf Diesel used peanut oil for developing fuel for the diesel engine (Hanna et al., 1999). In the 1930’s and 1940’s, vegetable oil (like peanut oils) was used in diesel, but only during critical situations like the Second World War (Meher et al., 2006).
1.2 Health Impacts

Diesel engine exhaust emissions, also known as 'diesel fumes', are a mixture of gases, vapors, liquid aerosols and substances made up of particles. They contain the products of combustion including carbon (soot), nitrogen, water, carbon monoxide, aldehydes, NO₂, SO₂, and polycyclic aromatic hydrocarbons. Diesel engines emit a significant amount of NOₓ, PM, and forty other toxic air contaminants into the atmosphere (American Lung Association, 1998). The carbon content varies from 60% to 80% depending upon the type of fuel used and also the engine type. Generally, the exhaust emissions depend upon the quality of the diesel fuel, type of engine, state of engine tuning, workload demand on the engine, engine maintenance and engine temperature.

Exposure to diesel fumes causes irritation of eyes or respiratory tract and other environmental effects (Table-1.1). Some effects are generally considered short term effects and disappear when moved away from the source. However, when the same exposure is considered for a long term process, it could lead to coughing, asthma and breathlessness. Continuous exposure to the fumes over a period of about 20 years increases the risk of lung cancer (Environmental Protection Agency).

<table>
<thead>
<tr>
<th>Acute (short-term exposure) Effects</th>
<th>Chronic (long-term exposure) Effects</th>
<th>Environmental Effects</th>
<th>Possible Improvements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irritation of eyes, nose, and throat</td>
<td>Lung cancer</td>
<td>Ozone formation</td>
<td>Use of cleaner-burning and renewable fuels (natural gas, propane, electricity)</td>
</tr>
<tr>
<td>Cough, headache, dizziness, nausea, and reduce lung function in children</td>
<td>Bronchitis</td>
<td>Acid rain</td>
<td>Retro-fitting of existing engines with particle filters</td>
</tr>
</tbody>
</table>
Heartburn, chest tightness, wheezing, vomiting, and increase the frequency of asthma attacks

Respiratory and heart diseases

Global climate change

Use of new diesel engines of advanced technologies that produce 90% lesser particle emissions

Damage of respiratory and central nervous system

Pneumonia

Visibility issues and haze

When exposed to higher levels: coma, convulsions, & death

Emphysema, & premature deaths

(Source: Compiled from U.S. EPA, Factsheet: USACHPPM)

1.3 Biodiesel Emissions

Biodiesel has been a solution at the critical verge of time when there was a fast depletion of energy resources. Biodiesel has exceptional properties compared to diesel. Biodiesel is developed from cooking oil and alcohol. Hence, when biodiesel is spilled it quickly gets degraded into natural organic residues. Biodiesel is no more toxic in nature than table salt and safe to handle. Biodiesel reduces nearly all forms of pollutants compared to petroleum diesel. Importantly, biodiesel reduces air toxics and cancer-causing compounds.

Biodiesel produces 78% less CO₂ compared to diesel. Biodiesel is developed from soybeans and various other vegetables that produce oils for cooking. These plants absorb CO₂ in the air and use them to build stems, leaves and seeds (which contain oils). The oil produced from these vegetables for the biodiesel is burnt and the left over plant material decomposes, returning the carbon from fuel and plant matter to the atmosphere as CO₂. This recycling of carbon from CO₂ in the atmosphere to carbon in plant material and back
to the atmosphere results in no accumulation of CO₂ in the atmosphere (Figure-1.1). Therefore, it does not contribute to the global climate change. Carbon dioxide from the petroleum fuels used for fertilizer, farm equipment, or transportation during biodiesel production accumulates in the atmosphere year after year. As a result, biodiesel produces 78% less CO₂ than diesel fuel. Biodiesel produces 2661 grams of CO₂ per gallon, compared to 12,360 grams per gallon for petroleum diesel fuel.

Figure-1.1: Recycling process of CO₂

Source: Biofuels – Biodiesel Clean, Green Diesel Fuel
1.4 EPA Research & Regulations

In 1990, the Clean Air Act Amendment (CAA) introduced fuel along with engine technology to be a potential source for the reducing toxic emissions. The increased concern among people with the rising of these toxic emissions has made many countries lay stringent rules. USEPA in 2006 has introduced a law where all the on-road diesel vehicles in the USA use ULSD. Law 11.097/2005 in Brazil similarly established minimum percentages to mix diesel and biodiesel, besides monitoring on the introduction of this new fuel into the market. According to 2008 Brazilian law, two percent biodiesel blending was mandatory, which increased by five percent starting in 2003 (Brazil Law 11.097/2005). EPA has reduced the standards of sulfur content present in diesel and gasoline to 15 parts per million (ppm) since 2007.

These stringent rules laid by the EPA have created awareness and made a need to switch to cleaner burning fuels. The state of Minnesota began blending two percent biodiesel into nearly all the state’s diesel fuel in 2005 and came up with ULSD which had lubricating properties inferior to those of the previously used #2 diesel.

A summary of U.S. air pollution control acts established by the EPA over recent years have been tabulated in Table-1.2 below.

<table>
<thead>
<tr>
<th>Federal Acts</th>
<th>Addressed Issues</th>
</tr>
</thead>
<tbody>
<tr>
<td>1955</td>
<td>First Air Pollution Act, to address national environmental problem of air pollution</td>
</tr>
<tr>
<td>1963</td>
<td>First Clean Air Act, to strengthen and accelerate programs for the prevention and abatement of air pollution</td>
</tr>
<tr>
<td>1965</td>
<td>Motor Vehicle Air Pollution Control Act to establish standards for automobile emissions</td>
</tr>
<tr>
<td>1966</td>
<td>Expanded local air pollution control programs</td>
</tr>
<tr>
<td>Year</td>
<td>Event</td>
</tr>
<tr>
<td>------</td>
<td>-------</td>
</tr>
<tr>
<td>1967</td>
<td>Air Quality Act, national emissions standards for stationary sources</td>
</tr>
<tr>
<td>1969</td>
<td>Extended research on low emission fuels and automobiles</td>
</tr>
<tr>
<td>1970</td>
<td>National Ambient Air Quality Standards, to protect public health and welfare, and regulate emissions of new source entering an area</td>
</tr>
<tr>
<td>1977</td>
<td>First attempt to prevent destruction of stratospheric ozone</td>
</tr>
<tr>
<td>1990</td>
<td>Emissions trading and reduction of sulfur using low-sulfur fuels as well as alternative fuels</td>
</tr>
<tr>
<td>1992</td>
<td>Energy Policy Act, to address energy efficiency and encourage fleets to use alternative fuels</td>
</tr>
<tr>
<td>1998</td>
<td>Energy Conservation Reauthorization Act, to allow agencies and alternative fuel providers to purchase alternative fuel vehicles</td>
</tr>
<tr>
<td>2001</td>
<td>The Highway Diesel Rule, effective from 2007, the sulfur content in diesel fuel to be reduced by 97%</td>
</tr>
<tr>
<td>2005</td>
<td>Energy Policy Act, federal tax credits for energy efficient products such as electric vehicles, ethanol, biodiesel</td>
</tr>
</tbody>
</table>

Source: (www.epa.gov)

There are a few standards on the emissions that are laid down by the EPA known as the National Ambient Air Quality (NAAQS) for pollutants considered being harmful to public health and the environment. The Clean Air Act (CAA) which was amended in 1990 requires EPA to set these standards and has established two types of national air quality standards. **Primary Standards** which are set to protect public health, including the health of "sensitive" populations such as asthmatics, children, and the elderly. **Secondary standards** set limits to protect public welfare, including protection against decreased visibility, damage to animals, crops, vegetation, and buildings.

The EPA Office of Air Quality Planning and Standards (OAQPS) has set National Ambient Air Quality Standards for six principal pollutants, which are called "criteria" pollutants. They are listed in Table-1.3. Units of measure for the standards are parts per million (ppm) by volume, parts per billion (ppb - 1 part in 1,000,000,000) by volume,
milligrams per cubic meter of air (mg/m$^3$), and micrograms per cubic meter of air (µg/m$^3$).

Table 1.3: National Ambient Air Quality Standards (U.S. EPA)

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Primary Standards</th>
<th>Secondary Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Level</td>
<td>Averaging Time</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9 ppm (10 mg/m$^3$)</td>
<td>8-hour</td>
<td>None</td>
</tr>
<tr>
<td>35 ppm (40 mg/m$^3$)</td>
<td>1-hour</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.15 µg/m$^3$</td>
<td>Rolling 3-Month</td>
<td>Same as Primary</td>
</tr>
<tr>
<td>1.5 µg/m$^3$</td>
<td>Average</td>
<td></td>
</tr>
<tr>
<td>Nitrogen Dioxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>53 ppb</td>
<td>Annual (Arithmetic Average)</td>
<td>Same as Primary</td>
</tr>
<tr>
<td>100 ppb</td>
<td>1-hour</td>
<td>None</td>
</tr>
<tr>
<td>Particulate Matter (PM$_{10}$)</td>
<td>150 µg/m$^3$</td>
<td>24-hour</td>
</tr>
<tr>
<td>Particulate Matter (PM$_{2.5}$)</td>
<td>15.0 µg/m$^3$</td>
<td>Annual (Arithmetic Average)</td>
</tr>
<tr>
<td></td>
<td>35 µg/m$^3$</td>
<td>24-hour</td>
</tr>
<tr>
<td>Ozone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.075 ppm (2008 std)</td>
<td>8-hour</td>
<td>Same as Primary</td>
</tr>
<tr>
<td>0.08 ppm (1997 std)</td>
<td>8-hour</td>
<td>Same as Primary</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>0.12 ppm</td>
<td>1-hour</td>
</tr>
</tbody>
</table>

Source: (USEPA- http://www.epa.gov/air/criteria.html)

1.5 MSDS of Biodiesel

ASTM PS 121 (Tables-1.4 & 1.5) provides the standards to ensure good fuel quality. PS 121 is a provisional standard; a final standard became available by winter of 2001. The standard is independent of any manufacturing process or feedstock. ASTM PS 121 is designed to ensure that biodiesel has the fuel properties for safe operation in a compression ignition engine and ensures that poor processing has not contaminated the fuel with products that will create engine damage.

Key fuel-quality issues are described below:

1) Biodiesel flash point is typically high (greater than 150 °C). FAMEs are not volatile. The limit for D93 is set at 100°C to ensure that the manufacturer has removed excess methanol used in the manufacturing process. Residual methanol in the fuel is a safety issue because very small amounts reduce the flash point. Methanol can also affect fuel pumps, seals, elastomers, and can result in poor combustion properties.

2) The sulfated ash test ensures the removal of all the manufacturing catalysts. High levels of manufacturing catalysts in the fuel can result in injector deposits or filter plugging.
3) Acid numbers will become elevated if the fuel ages, or if it was not properly manufactured.

4) Acid numbers higher than 0.10 have been shown to be associated with fuel system deposits, and reduce the life of fuel pumps and filters.

Table-1.4: Selected Fuel Properties for Diesel and Biodiesel Fuels

<table>
<thead>
<tr>
<th>Fuel Property</th>
<th>Diesel</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide</td>
<td>-43.2%</td>
<td>-12.6%</td>
</tr>
<tr>
<td>Fuel Standard</td>
<td>ASTM D975</td>
<td>ASTM PS121</td>
</tr>
<tr>
<td>Fuel Composition</td>
<td>C10-C21 HC</td>
<td>C12-C22 FAME</td>
</tr>
<tr>
<td>Lower Heating Value, Btu/gal</td>
<td>131,295</td>
<td>117,093</td>
</tr>
<tr>
<td>Kin. Viscosity, @ 40°C</td>
<td>1.3-4.1</td>
<td>1.9-6.0</td>
</tr>
<tr>
<td>Specific Gravity kg/l @ 60°F</td>
<td>0.85</td>
<td>0.88</td>
</tr>
<tr>
<td>Density, lb/gal @ 15°C</td>
<td>7.079</td>
<td>7.328</td>
</tr>
<tr>
<td>Water, ppm by wt.</td>
<td>161</td>
<td>0.05% max</td>
</tr>
<tr>
<td>Carbon, wt. %</td>
<td>87</td>
<td>77</td>
</tr>
<tr>
<td>Hydrogen, wt. %</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>Oxygen, by diff. wt. %</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>Sulfur, wt. %</td>
<td>0.05 max</td>
<td>0-.0024</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>188 to 343</td>
<td>182 to 338</td>
</tr>
<tr>
<td>Flash Point</td>
<td>60 to 80</td>
<td>100 to 170</td>
</tr>
<tr>
<td>Cloud Point</td>
<td>-15 to 5</td>
<td>-3 to 12</td>
</tr>
<tr>
<td>Pour Point</td>
<td>-35 to -15</td>
<td>-15 to 16</td>
</tr>
<tr>
<td>Cetane Number</td>
<td>40 to 55</td>
<td>48 to 60</td>
</tr>
<tr>
<td>Autoignition temperature</td>
<td>316</td>
<td></td>
</tr>
<tr>
<td>Property</td>
<td>ASTM Method</td>
<td>Limits</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>-------------</td>
<td>----------------</td>
</tr>
<tr>
<td>Stoichiometric Air/Fuel Ratio, wt./wt.</td>
<td></td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.8</td>
</tr>
<tr>
<td>BOCLE Scuff, grams</td>
<td></td>
<td>3,600</td>
</tr>
<tr>
<td>HFRR, microns</td>
<td></td>
<td>685</td>
</tr>
</tbody>
</table>

(Source: MSDS of biodiesel)

Table-1.5: ASTM PS 121 Biodiesel for B20

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM Method</th>
<th>Limits</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash Point</td>
<td>D93</td>
<td>100.0min</td>
<td>Degrees C</td>
</tr>
<tr>
<td>Water &amp; Sediment</td>
<td>D2709</td>
<td>0.050max.</td>
<td>% vol.</td>
</tr>
<tr>
<td>Kinematic Viscosity, 40 C</td>
<td>D445</td>
<td>1.9 – 6.0</td>
<td>Mm²/sec.</td>
</tr>
<tr>
<td>Sulfated Ash</td>
<td>D874</td>
<td>0.020max.</td>
<td>% mass</td>
</tr>
<tr>
<td>Sulfur</td>
<td>D5453</td>
<td>0.0015max.</td>
<td>% mass</td>
</tr>
<tr>
<td>Copper Strip Corrosion</td>
<td>D130</td>
<td>No. 3 max.</td>
<td></td>
</tr>
<tr>
<td>Cetane Number</td>
<td>D613</td>
<td>46 min.</td>
<td></td>
</tr>
<tr>
<td>Cloud Point</td>
<td>D2500</td>
<td>Report to customer</td>
<td>Degree C</td>
</tr>
<tr>
<td>Carbon Residue, 100% sample</td>
<td>D4530**</td>
<td>0.050max.</td>
<td>% mass</td>
</tr>
<tr>
<td>Carbon Residue, Ramsbottom</td>
<td>D524</td>
<td>0.090max.</td>
<td>% mass</td>
</tr>
<tr>
<td>Acid Number</td>
<td>D664</td>
<td>0.80max.</td>
<td>Mg KOH/gm</td>
</tr>
<tr>
<td>Free Glycerin</td>
<td>D6584</td>
<td>0.020max.</td>
<td>% mass</td>
</tr>
<tr>
<td>Total Glycerin</td>
<td>D6584</td>
<td>0.240max.</td>
<td>% mass</td>
</tr>
<tr>
<td>---------------</td>
<td>-------</td>
<td>-----------</td>
<td>--------</td>
</tr>
</tbody>
</table>

(Source: MSDS of biodiesel)

5) Free and total glycerin numbers measure the complete conversion of the fats and oils into the FAMEs. If these numbers are too high, the manufacturing process is inadequate and engine fouling will occur. **Never** use fuel that exceeds the free and total glycerin limit. Return the fuel to the fuel provider.

6) Oxidative stability test methods are under development which will allow a customer to determine if the fuel will remain stable in storage over extended periods of time and to test fuels to determine if they have degraded during storage. ASTM PS 121 does not contain any test methods for stability at this time. High acid numbers coupled with high viscosity numbers indicate a degraded fuel.

7) Cloud point does not have a limit, but should be reported to the customer. Cold filter plug point is a more accurate test of biodiesel’s cold weather performance. If one is using a biodiesel blend, an accurate estimate of how the biodiesel will perform in the winter months will require mixing the biodiesel with the winter diesel typically delivered in one’s area and testing the mixture.

8) Biodiesel generally contains less than 15 ppm sulfur and the test for low sulfur fuel (ASTM D 5453) should be used for accurate results instead of D 2622.

9) Biodiesel requires the Cetane Number test because the Cetane Index test methods provide inaccurate results.

10) The aromatics test for diesel fuel will provide inaccurate results for biodiesel. Biodiesel does not contain any aromatics.
11) Biodiesel should be clear, although it may come in a variety of colors. Biodiesel color does not predict fuel quality.

12) A milky layer of material on the bottom of a fuel tank can have several meanings. If the fuel was frozen or chilled, the layer may contain the saturated FAMEs with high cloud points. If the material returns to a clear form after heating to 100 °F, it is probably composed of biodiesel saturates. If the material remains milky or jelly-like at 100 °F, it may be poorly processed fuel residues, water, or other contaminants and the fuel shipment should be returned to the manufacturer.
Chapter 2

Literature Review

The majority of world’s energy source excepting hydroelectricity and nuclear energy are supplied through petrochemical sources, coal, and natural gas. With the current pace of consumption these sources of oil will soon be exhausted; oil being a finite source cannot be recycled (Laherre’re et al., 1995 and 1996). There is an immediate concern to find new alternative fuels before these reserves become a word of the past. These concerns raised an idea of using animal fats and vegetable oils for fuel production and as an alternative for diesel fuel mainly keeping environmental considerations in mind. However, some of the physical and chemical properties such as high viscosity and high molecular weight cause poor fuel atomization and low volatility, leading to incomplete combustion and in the long run to severe engine deposits, injector coking and piston ring sticking (Bagby et al., 1987). In spite of these implications there was an effort to develop an application to use straight vegetable oil in automotive vehicles (Reyes et al., 2003).
Biodiesel is an alternative diesel fuel produced by transesterification of vegetable oil, animal fats or waste cooking oils using alcohol and a catalyst to give the corresponding fatty acid methyl esters (Zhang et al., 2003; Dorado et al., 2002; Zhen et al., 1996; Williams et al., 2002). The process of transesterification removes glycerol from the triglycerides and replaces it with radicals from the alcohol used for the conversion process and forms monoesters. This process decreases the viscosity but maintains the heating value and cetane number. These monoesters are called as biodiesel (Kusy et al., 1982).

Biodiesel can not only be used in the neat form but also can be mixed with petroleum diesel fuel in any unmodified diesel engine (Canakci et al., 2001). Biodiesel commercial production started out first using rapeseed oil methyl ester in 1988 (Korbitz et al., 2001). To date, biodiesel is prepared in 28 countries with Germany and France as pioneers and the major producers in Europe (Kusdiana et al., 2000); however there are still some technical problems which limit the cost of biodiesel. On the other hand, an estimate by the United States Department of Energy showed that up to 50% of total diesel fuel could be potentially replaced by biodiesel. Biodiesel production from vegetable oil and animal fats in USA is currently over 7,000,000 cubic meters per year (Alca´ntara et al., 2000). Compared to diesel, biodiesel provides comparable fuel efficiency, torque and horsepower (Bunger et al., 1998 and 2000). Diesel fuel contains different hydrocarbons (benzene, toluene, xylenes, etc.), sulfur and contamination of crude oil residues (Klass et al., 1998). But chemical composition of biodiesel is different from the petroleum-based diesel fuel. Biodiesel reduces PM, carbon monoxide (CO) and increases NOx emissions
Biodiesel hydrocarbon chains are generally 16–20 carbons in length and contain oxygen at one end. Biodiesel does not contain any sulfur, aromatic hydrocarbons, metals and crude oil residues (Keskin et al., 2004). Biodiesel contains 11% of oxygen by weight. These properties improve combustion efficiency and emission profile. The fuel oxygen allows the fuel to burn more completely, so fewer unburned fuel emissions may result. The same phenomenon reduces air toxics, which are associated with the unburned or partially burned HC and PM emissions.

Testing has shown that PM, HC, and CO reductions are independent of the biodiesel feedstock (Biodiesel handling user guide, 2009). Emission impacts of 20% volume of biodiesel for soy-bean based biodiesel added to an average base fuel showed a change of -10.1% change in emissions for PM, -21.1% for HC, and -11% for CO (EPA, 2002). The most important part is the reduction of CO$_2$ which is the most important sponsor of greenhouse effect. When biodiesel is made from vegetable oil, the crops absorb CO$_2$ for their growth which ultimately reduces enormous CO$_2$ production compared to fuels developed using the fossil fuels. And since biodiesel is a carbon-neutral product it does not develop additional CO$_2$ to the environment (Scharmer et al., 1998; Mc Donnell et al., 1999).

PM was reported to be one of the most dangerous among air pollution even at unexpectedly low concentrations (Pope et al., 2000). Particulate matter are an air-suspended mixture of solid and liquid particles which vary based on size, shape, surface area, chemical composition, origin and solubility. The particles are divided into coarse particles, fine particles, and ultrafine particles based on their size distribution. The
particles are trimodal under ambient air (Chow et al., 1995). Coarse particles are derived primarily from suspension or resuspension of soil, dust, mining, farming, tornados, storms, and so forth. Coarse particles also include mold, spores, pollens, and sea salts. Coarse particles are often indicated by mass concentrations of particles which are greater than 2.5-µm. Fine particles are derived primarily from direct emissions from combustion processes, such as vehicle use of gasoline, diesel, wood burning, coal burning for power generation, and industrial processes, such as smelters, cement plants, paper mills, and steel mills. Fine particles also consist of transformation products, which are generated by conversion from primary sulfur and nitrogen oxide emissions and secondary organic aerosol from volatile organic compound emissions. Fine PMs are indicated with particles of aerodynamic diameter less than or equal to a 2.5-µm (Pope et al., 2006). Ultrafine particles are typically defined as particles with an aerodynamic diameter < 0.1 µm (EPA and Oberdorster et al., 2005). Ambient air in urban and industrial environments is constantly receiving fresh emissions of ultrafine particles from combustion related sources, such as vehicle exhaust and atmospheric photochemical reactions (Kulmala et al., 2003; Watson et al., 2006). These primary ultrafine particles, however, have a very short life (minutes to hours) and rapidly grow (through coagulation and/or condensation) to form larger complex aggregates but typically remain as part of PM2.5.

Particulate matter consists of soot, dust, tiny objects of liquid and other material. These particles enter the body through various locations and cause various problems to the body. Initial effects would be cough, excess phlegm and wheeze which develop into long-term diseases like asbestosis, mesothelioma and lung cancer. Generally particles
which are greater than PM10 are trapped in the upper part of the respiratory tract, PM < 10 µm enter the tracheobronchial region while the parts less than PM 2.5 get accumulated in the remote locations of lungs. It is very dangerous as the particles get accumulated into the body (EPA). Biodiesel reduces these PM due to presence of oxygen which provides better combustion. As the blend concentration increases the number of particulate matter reduces.

Biodiesel reduces cancer causing compounds, using a pure biodiesel can reduce the risk of cancer by 94%; whereas by using B20 we can reduce the carbon causing compounds by 27%. Also biodiesel consists of 0-24 ppm sulfur, significantly reducing the production of SO₂ compounds. B20 has 20% more benefits compared to pure biodiesel. It reduces the soot and smell of diesel exhaust (U.S. Dept of Energy, 2001).

Several studies have shown the performance of diesel engines fueled with different types of biodiesel such as sunflower oil methyl ester, sunflower oil ethyl ester, rapeseed oil methyl ester, sunflower oil ethyl ester, palm oil methyl ester, and palm oil ethyl ester, waste frying oil biodiesel from different oil seed and olives (Mittelbach et al., 1998; Chancellor et al., 1981; Dorado et al., 2003). There have been also engine tests using biodiesel made from soybean oil (Moreno et al., 1999; Chang et al., 1996). These studies have revealed that 37% of carbon portion of the particulates decreased, also there was a significant reduction in carbon monoxide and unburned hydrocarbons. Oxides of nitrogen were observed to increase by 12% and there was a 25% decrease on the total particulate matter emitted. Biodiesel improves the lubricating effect which results in longer engine component life (Boehman et al., 2005; Kinast et al., 2001; Gerpen et al., 2005). The flash
point of biodiesel is higher compared to diesel fuel. Although the flash point does not affect the combustion directly it makes biodiesel safer regarding the storage and transport (Encinar et al., 2005; Owen et al., 1995).

There are a few disadvantages with biodiesel: compared to diesel biodiesel has a higher price due to use of virgin vegetable oils which are costly (Felizardo et al., 2006). This cost can be reduced by the usage of less expensive feed stocks. Possible sources for these feedstock’s are waste oils and greases from restaurant and rendered animal fats (Canakci et al., 2003). Another disadvantage of biodiesel is due to the cold flow properties of biodiesel being poor it may cause problems to start the engine during the winter and hence limit the use of biodiesel during winter (Knothe et al., 2005).

Previous studies involving TARTA transit buses equipped with MBE and Cummins engines were studied for emissions under on-road and idle engine conditions showed that emissions increased as blend increased under idle engine conditions. Also from the studies it was observed that on road emissions showed CO emissions reduced as percentage of blend increased from B0 to B20. The reduction was 38% for MBE engines, 22% for Cummins engines tested. NOx emission was found to increase from 15% for MBE engines and 10% for Cummins engines. CO2 emissions reduced by 11% for MBE engines and 23% for Cummins engines and SO2 was 5% decrease for MBE engines. For idle conditions it was observed that CO2 emissions reduced by 2% for B0 to B5 and 21% for B5 to B10 and 4% for B10 to B20. An increase of 128% for CO emissions and 121% of SO2 emissions for B0 to B20 was observed (TARTA 3-Year Composite Draft). Also, Nerella and Kumar (2009-2010) have discussed the variation of exhaust emissions with
engine type. Under cold-start emission of NOx, SO2, and CO2 were observed to increase irrespective of the biodiesel blend. Study of exposure to commuters in TARTA buses tested for 8-hour period revealed that, the mean 8-hour exposure to carbon dioxide and sulfur dioxide to be significantly higher inside ULSD buses as compared to B20 fueled buses, while the carbon monoxide and nitric oxide concentrations were higher inside B20 buses. Nitrogen dioxide and particulate matter are found to be statistically similar for both the buses (Kadiyala et al., 2008). Vijayan (2007) compared indoor and outdoor concentrations simultaneously and observed outdoor concentrations to be strongly influencing the indoor concentrations and outdoor concentrations to be consistently higher than the indoor concentrations during the runs. The results also showed that the PM1.0 mass comprised of around 40% particles between 0.30-0.40 μm, 25% particles between 0.40-0.50 μm and 35% particles between 0.50 and 1.0 μm in diameter. A detailed analysis on the particle shape, size, and aspect ratio was done by Shandilya and Kumar (2010). Ultrafine mode was observed to be near 0.1μm and the coarse mode beyond 0.3μm. The uni-modal and bi-modal peak lies in the ultrafine mode region. Multimode peaks were found mostly in the coarse mode region. Most of the particle shapes were oblong and square. The average aspect ratio of indoor particles was 2.4-3.6 for the biodiesel bus and 2.3-2.9 for the ULSD bus.
Chapter 3

Problem Statement & Objective

3.1 Problem Statement

Biodiesel reduces the concentration of harmful gas components but does not complete eradicate the problem. Biodiesel also releases certain percentage of harmful gas emissions which are dangerous to the human life. In this study, the possible combinations were to be identified at which minimum concentrations of each emission gas component for tested biodiesel blends can be attained.

A laboratory study was used because, even though many case studies have been done for on-road emissions, it is not always possible to test accurately under a natural environment. Many assumptions were made to overcome these factors. In the laboratory, however, the experiments can be carried out under required environmental factors. Many effects can be maintained constant while the specific effect that we are interested in can be observed. The experiments can be carried out without any restrictions of surrounding conditions.
3.2 Objective

The objective of this research was to find out the emissions for biodiesel blends B5, B10, B50, and compare them with the blends, B20 and ULSD and check for the possible combination to reduce the each emission gas component. Emissions were collected at different combinations of temperatures, 500 °F and 550 °F and pressures at, 500 psi and 550 psi.

As the ignition temperature of biodiesel was 351 °F (MSDS of Biodiesel), the biodiesel was expected to ignite at the same temperature.
4.1 Working of a Diesel Engine

There are two main types of internal-combustion engines. One type, found in most motor cars, is called a spark-ignition engine. It uses electricity and spark plugs to ignite the fuel in the engine's cylinders. The other type, the diesel engine, is a compression-ignition engine. When air confined in a cylinder is suddenly compressed, the temperature of the air rises. In a diesel engine, each piston compresses air in a cylinder. Fuel is injected and forms an explosive mixture, which ignites spontaneously under pressure.

Diesel engines burn fuel oils, which require less refining and are cheaper than higher-grade fuels such as gasoline. During the combustion process, the stored chemical energy in the fuel is converted to thermal, or heat, energy. The temperature in each cylinder rises as high as 2,480 °C and creates pressures of about 100 kilograms per square centimetre (1420 psi).
The pressure pushes against the tops of the pistons, forcing them to the other end of their cylinders. The pistons are connected by a rod or other suitable connecting mechanism to a crankshaft which they turn. In this way, a diesel engine supplies rotary power to drive vehicles and other kinds of machines.

In order for the compressed air inside the cylinders to ignite the fuel, it must have a certain temperature. The degree to which the temperature of the air rises depends on the amount of work done by the piston in compressing it. This work is measured in terms of the ratio between the volume of uncompressed air and the volume of the air after it is compressed.

The compression ratio necessary to ignite the fuel depends on the size of the engine's cylinders. In large cylinders, the compression ratio is about 13 to 1. For small cylinders, it may be as high as 20 to 1. The average is 14.5 to 1. Near the end of the piston's compression stroke, the fuel is injected into a cylinder. In order to have the fuel and air mix well, the fuel is injected under high pressure as a spray. Combustion usually starts just before the piston ends its compression stroke. The power of diesel engines can be increased by supercharging. This is the technique of forcing air under pressure into the cylinders (www.thinkquest.org). Figure-4.1 shows the schematic description of diesel operation.
4.2 Procedure

Using the methodology of a real time diesel engine working, a procedure was developed for the experiments. The real-time compression-ignition engine procedure was applied. The procedure described below was largely dictated by the small amounts of fuel used for testing. An auto-clave batch reactor for experimental purposes was used. The tests were carried out for each biodiesel blend with varying temperatures and pressures.

A known amount of biodiesel was placed in the batch reactor. The desired temperature was set using an Omega I-series temperature controller with an Omega solid state relay. The temperature inside the reactor was identified using a thermocouple. As the temperature was steadily increasing an external pressure was applied inside the reactor using helium gas. The pressure inside the reactor was identified using a pressure detector.
Once the temperature started building up, the pressure inside the reactor started to build up, which indicated the initial warming up of biodiesel. As the temperature reached its ignition point there was a sudden rise in the pressure and temperature simultaneously which indicated the biodiesel reached its ignition point. The reaction was then run for a couple of hours before it was released using the pressure relief regulator. The gas was allowed to pass through the filter paper. As the emissions passed through the PTFE filter paper, the particulate matter of sizes greater than 4 µm were trapped in the filter paper. Particulate matter with size lower than 4 µm was trapped in a high capacity filter unit.

The gas was allowed to pass through the filter paper into a GC. Once the gas was collected in the GC, the emissions were analyzed for the concentrations of CO, H₂, N₂, CO₂, and CH₄. Simultaneously using the SEM analysis the filter papers were analyzed to get the detailed analysis of the particulate matter with respect to particle size, distribution, and appearance. The same procedure was applied for ULSD with varying temperatures and pressures.
Chapter 5

Sample Preparation and Equipment

5.1 Test Fuels

Biodiesel and ULSD required for the experiments were obtained from the Toledo Area Regional Transit Authority (TARTA), Toledo, Ohio. The biodiesel used was made from soy-beans. ULSD, B20, and B100 were obtained from TARTA. The biodiesel was then mixed with diesel to get the required grades using the B100.

5.2 Equipment

All the experiments were carried out in a 1.75 cm-inside diameter and 45 cm long stainless steel tubular reactor. The reactor tube was placed in a furnace (Applied Test Systems, Inc.). The reaction temperature was monitored using a K-type thermocouple inserted into the reactor tube. The temperature was controlled using an Omega temperature controller (SSRDIN660DC25 and CNi16D44-C4EI). For the reaction, to take place pressure was developed inside the reactor using He gas (Sadashiv et al., 2006).
A Shimadzu 2010 gas chromatograph, equipped with both a PDHID (pulsed discharge helium ionization detector) and an FID (flame ionization detector) was used for real-time analysis. A polycarbonate filter paper of 47mm size was used to collect PM.

Figure-5.1: Schematic diagram of the procedure of experiment
Chapter 6

Type of Data Collected

The emissions collected from the batch reactor were sent through 47mm PTFE filter papers. Particulate matter was collected from the emissions on these filter papers. The particulate matter was allowed to settle on the filter paper till all the emission was drained out. The emissions leading out of the filter paper casing were passed into the GC for gas analysis. After the gas analysis all the emissions were disposed out into the hood.

6.1 Gas Chromatography Analysis

The flue gases were then routed to the gas chromatography (GC) for compositional analysis. A small amount of gas samples (approximately 250μl) was injected into the column. GC collects the gas and passes it through a PDHID detector. GC uses three carrier gases (air, hydrogen, and helium) for its analysis. The emissions mix with the carrier gas and pass through the detector. The column elutes different gases at different time periods depending upon the affinity of a gas to the stationary phase with temperature program. Eluents (here individual gases) from the column were ionized by photons from
the helium discharge zone. Resulting electrons were focused towards the collector electrode by the bias electrode which in return produces a current signal. Y-axis in the GC plots represents the intensity of this current produced.

The GC uses EZ-start software to plot a user-friendly graphical graph with, time on x-axis and intensity on the y-axis. The graph consisted of peaks which indicated the area of each gas component present in gas sample emitted from the combustion of the blend. In the emissions produced from each experiment CO, H₂, N₂, CH₄, and CO₂ were the gas components measured. For accurate results, the analysis was done several times to check the variations of the peaks.

The concentrations of these gas components present in the emissions of the each biodiesel blend at different temperature and pressure combinations were measured with the GC. After all the graphs were obtained the analysis process was started. In this process, each gas component of ultra high purity was sent and the analysis was done. The areas of each gas were inputted into a spreadsheet and a parabolic graph was developed. From the graph, a regression equation was acquired into which the unknown areas were inputted and concentrations were calculated.

6.2 PM Analysis

The filter papers for each blend were analyzed using the SEM for particulate matter. Particle images were developed from the SEM which were later analyzed using ImageJ to collect the morphological data of particles from the images developed using SEM. Each
filter paper was placed in the SEM and was analyzed separately based on blend categorization. For accurate results, the filter paper was sputter coated with palladium-gold plating before it was analyzed.
Chapter 7

Results & Discussion

At first, the emissions were passed through the filter paper which collects particulate matter required for the SEM analysis. The gas was then sent to the GC for the gas analysis.

7.1 Gas Chromatography Analysis

The graphs obtained from the GC observed for each blend at a particular temperature and pressure range are located in the appendix of this research. In the graphs obtained, the first peak represented H$_2$, followed by CO, then N$_2$, CH$_4$, and CO$_2$. Tables-7.1 & 7.2, show the observed peak areas for different gas components for each blend under different engine conditions tested. To calculate the concentrations of these different emissions, analysis was done. For the analysis purpose pure gases were sent into the GC.
Different gases emission intensities for the blends at various temperatures and pressures

Table 7.1: Emissions of different blends from GC

<table>
<thead>
<tr>
<th>Blend</th>
<th>Temperature, Pressure</th>
<th>GC peak size (mVolts)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H₂</td>
</tr>
<tr>
<td>B5</td>
<td>500°F, 300psi</td>
<td>1434316</td>
</tr>
<tr>
<td></td>
<td>500°F, 350psi</td>
<td>343515</td>
</tr>
<tr>
<td></td>
<td>550°F, 300psi</td>
<td>1018493</td>
</tr>
<tr>
<td></td>
<td>550°F, 350psi</td>
<td>1251203</td>
</tr>
<tr>
<td>B10</td>
<td>500°F, 300psi</td>
<td>810130</td>
</tr>
<tr>
<td></td>
<td>500°F, 350psi</td>
<td>876852</td>
</tr>
<tr>
<td></td>
<td>550°F, 300psi</td>
<td>3868354</td>
</tr>
<tr>
<td></td>
<td>550°F, 350psi</td>
<td>913908</td>
</tr>
<tr>
<td>B50</td>
<td>500°F, 300psi</td>
<td>912629</td>
</tr>
<tr>
<td></td>
<td>500°F, 350psi</td>
<td>543026</td>
</tr>
<tr>
<td></td>
<td>550°F, 300psi</td>
<td>1562083</td>
</tr>
<tr>
<td></td>
<td>550°F, 350psi</td>
<td>590041</td>
</tr>
</tbody>
</table>

Compared to B20 and ULSD

Table 7.2: Emissions of different blends from GC

<table>
<thead>
<tr>
<th>Blend</th>
<th>Temperature, Pressure</th>
<th>GC peak size (mVolts)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H₂</td>
</tr>
<tr>
<td>B20</td>
<td>500°F, 300psi</td>
<td>1859615</td>
</tr>
<tr>
<td></td>
<td>500°F, 350psi</td>
<td>727127</td>
</tr>
<tr>
<td></td>
<td>550°F, 300psi</td>
<td>750414</td>
</tr>
<tr>
<td></td>
<td>550°F, 350psi</td>
<td>873229</td>
</tr>
<tr>
<td>ULSD</td>
<td>500°F, 300psi</td>
<td>1566986</td>
</tr>
<tr>
<td></td>
<td>500°F, 350psi</td>
<td>835046</td>
</tr>
<tr>
<td></td>
<td>550°F, 300psi</td>
<td>933590</td>
</tr>
<tr>
<td></td>
<td>550°F, 350psi</td>
<td>716123</td>
</tr>
</tbody>
</table>
The analysis was done using the calibration analysis method. For analysis purpose, known amount of gas component of 99.99% purity were sent into the GC. Two gases were sent at a time under a total flow rate of 200ml/min. The gas was sent in such a way that it would bisect the extreme ends of areas developed by the different blends. With these known flow rates, areas were calculated. From the known areas and concentrations a regression equation was developed. The test results of each gas component under the various conditions tested were then inputted into these regression equations and the concentrations were calculated (Table-7.3). Each blend was then compared to the results of B20 and ULSD. Figures-7.1 – 7.5 show the different regression equations by the gas components.

Figures-7.1 - 7.5 show the calibration curves for H₂, CO, N₂, CH₄, and CO₂ respectively.
Figure 7.2: Concentration vs. area for CO

\[ y = 3E-14x^2 + 3E-08x + 0.163 \]

\[ R^2 = 0.998 \]

Figure 7.3: Concentration vs. area for N\(_2\)

\[ y = 4E-14x^2 + 7E-07x - 0.058 \]

\[ R^2 = 0.999 \]
Figure 7.4: Concentration vs. area for CH4

\[ y = 5 \times 10^{-10}x + 2.832 \]
\[ R^2 = 0.998 \]

Figure 7.5: Concentration vs. area for CO2

\[ y = 3 \times 10^{-14}x^2 + 4 \times 10^{-07}x - 2 \times 10^{-14} \]
\[ R^2 = 1 \]
## Emission component concentration of each blend

Table-7.3: Emission concentration of different gas components of different blends from regression equation

<table>
<thead>
<tr>
<th>Blend</th>
<th>Temperature, Pressure</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H₂</td>
</tr>
<tr>
<td>ULSD</td>
<td>500F, 300psi</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>500F, 350psi</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>550F, 300psi</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>550F, 350psi</td>
<td>1.5</td>
</tr>
<tr>
<td>B5</td>
<td>500F, 300psi</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>500F, 350psi</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>550F, 300psi</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>550F, 350psi</td>
<td>2.8</td>
</tr>
<tr>
<td>B10</td>
<td>500F, 300psi</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>500F, 350psi</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>550F, 300psi</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>550F, 350psi</td>
<td>2.0</td>
</tr>
<tr>
<td>B20</td>
<td>500F, 300psi</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>500F, 350psi</td>
<td>1.6</td>
</tr>
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<tr>
<td></td>
<td>550F, 300psi</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>550F, 350psi</td>
<td>1.3</td>
</tr>
</tbody>
</table>
7.1.1 Effect of Blending

In this section, the concentrations of H$_2$ of different blends at a particular temperature and pressure were compared.

**H$_2$**

**T = 500 °F & P = 300 psi**

Under the above condition, it was observed that the concentrations of H$_2$ were observed to be the least for B10, while, B20 had higher H$_2$ emissions. The emissions of H$_2$ at 500 °F and 300 psi in general were found be higher when compared to the other conditions tested. ULSD had the highest H$_2$ emissions compared to the biodiesel blends.

![H2 Emission Concentrations](image)

**Figure-7.6: Comparison of H$_2$ emission concentrations for different blends at T = 500 °F & P = 300 psi**

**T = 500 °F & P = 350 psi**

Under the above condition, it was observed that the concentration were the least for all the blends. The low emissions indicate that H$_2$ emissions reduced at lower temperatures.
and higher pressures. In this condition, it was observed that B5 showed the least H\textsubscript{2} emissions and B10 showed high emissions of H\textsubscript{2}.

Figure-7.7: Comparison of H\textsubscript{2} emission concentrations for different blends at T = 500 °F & P = 350 psi

Figure-7.8: Comparison of H\textsubscript{2} emission concentrations for different blends at T = 550 °F & P = 300 psi
Under the above condition, lower H\textsubscript{2} emissions were observed. It was observed that, B20 had the lowest H\textsubscript{2} emissions whereas B10 had the highest H\textsubscript{2} emissions.

![Figure-7.9: Comparison of H\textsubscript{2} emission concentrations for different blends at T = 550 °F & P = 350 psi](image)

Under the above conditions, B50 had the least H\textsubscript{2} emissions. The highest H\textsubscript{2} emissions were observed for B5. The emissions were showing a decreasing trend as the biodiesel was increasing compared to ULSD under the above conditions.

Under a generalized view, the H\textsubscript{2} emissions were observed to be decreasing as the blend was increasing. Under lower temperatures and varying pressures biodiesel had lesser emissions compared to ULSD, whereas under higher temperatures and varying pressures ULSD had lesser emissions compared to Biodiesel. Considering any of the above conditions implemented each biodiesel attained the least H\textsubscript{2} emissions at a particular combination of temperature and pressure. Also from the above results, it shows that H\textsubscript{2} was observed to be lower under lower temperatures and higher pressures.
CO

$T = 500 \, ^\circ F \, \& \, P = 300 \, \text{psi}$

Figure 7.10: Comparison of CO emission concentrations for different blends at $T = 500 \, ^\circ F \, \& \, P = 300 \, \text{psi}$

Under the above conditions, B20 showed the least CO emissions and B10 showed the highest emissions of CO. Not much variation was observed for the different blends under low temperature and pressures.

$T = 500 \, ^\circ F \, \& \, P = 350 \, \text{psi}$

Under the above condition, tested ULSD showed the least CO emissions and B10 showed the highest emissions of CO. B5, B10, and B50 showed very high emissions compared to ULSD and B20.
Different blends were tested under the above conditions. ULSD showed the lowest CO emissions compared to biodiesel. B10 showed the highest CO emissions.
Figure 7.13: Comparison of CO emission concentrations for different blends at $T = 550\,^\circ F$ & $P = 350\,\text{psi}$

Under the above conditions, B20 showed the least CO emissions. B10 showed the highest CO emissions.

The blends were tested under the above conditions and it incurred that B10 had the highest CO emissions when compared to the other blends. If the CO emissions are high, it means that the blend hasn’t burnt properly which indicates that the blend under the above conditions could not attain complete combustion. B10 was observed to be the highest source for CO under the tested conditions. B20 showed lesser emissions of CO indicating its proximity to good combustion. The above graphs showed an increasing trend of CO from ULSD to B10 and a sudden decrease in B20 emissions, and again an increase for B50 indicating the conditions might be suitable for B20. Incomplete combustion indicates incomplete burning of the fuel leading to usage of more fossil fuels and producing less energy. From the graphs, it was found that CO emissions were lower
under low temperatures compared to high temperatures and also the pressure effects did not influence the CO emissions much.

$N_2$

$T= 500 \, ^\circ F \, \& \, P = 300 \, \text{psi}$

![Figure-7.14: Comparison of $N_2$ emission concentrations for different blends at $T = 500^\circ F \, \& \, P = 300 \, \text{psi}$](image)

$N_2$ emissions did not show much variation for all the blends tested for low temperatures and pressures. Under the above conditions, B5 showed the highest and B10 showed the least concentrations.

$T= 500 \, ^\circ F \, \& \, P = 350 \, \text{psi}$

Reduced emissions of $N_2$ were observed under the above tested conditions. Under the above conditions, deployed B5 showed the least and B10 showed the highest. Not much variation was found for different blends under lower temperatures.
Figure-7.15: Comparison of N\textsubscript{2} emission concentrations for different blends at T = 500 °F & P = 350 psi

Figure-7.16: Comparison of N\textsubscript{2} emission concentrations for different blends at T = 550 °F & P = 300 psi
Higher N₂ emissions were observed under the conditions tested above. ULSD compared to the biodiesel showed lower N₂ emissions. B50 had the highest N₂ emissions. An increasing trend was observed in a generalized view.

\[ T = 550 \, ^\circ F \text{ & } P = 350 \, \text{psi} \]

![Figure-7.17: Comparison of N₂ emission concentrations for different blends at T = 550 \, ^\circ F & P = 350 \, \text{psi}](image)

Lower emissions of N₂ were observed under the above tested conditions. B20 showed the least of N₂ emissions compared to the other blends and B50 had the highest N₂ emissions. An increasing trend was observed from the above results.

N₂ showed a varying trend of emissions for all the blends tested. Lower emissions were observed under higher pressures and lower temperatures. Under higher temperatures and varying pressures, increasing trends of N₂ emissions were observed. Not much variation in the concentrations of N₂ emissions was observed between the blends under the above tested conditions. Under lower temperatures, N₂ emissions from biodiesel did not play a
significant role but under high temperatures and pressures N\textsubscript{2} emissions were significantly low for biodiesel than ULSD.

\textbf{CH\textsubscript{4}}

\begin{itemize}
  \item T= 500 °F & P = 300 psi
\end{itemize}

![Figure-7.18](image1)

Figure-7.18: Comparison of CH\textsubscript{4} emission concentrations for different blends at T = 500 °F & P = 300 psi

\begin{itemize}
  \item T= 500 °F & P = 350 psi
\end{itemize}

![Figure-7.19](image2)

Figure-7.19: Comparison of CH\textsubscript{4} emission concentrations for different blends at T = 500 °F & P = 350 psi
Figure-7.20: Comparison of CH₄ emission concentrations for different blends at T = 550 °F & P = 300 psi

Figure-7.21: Comparison of CH₄ emission concentrations for different blends at T = 550 °F & P = 350 psi
Less variation in CH₄ concentrations were observed for all the blends under the above tested conditions. CH₄ on comparing all the conditions showed lower emissions at low temperatures and high pressures which may give an implication that it decreases at lower temperatures and higher pressures.

CO₂

T= 500 °F & P = 300 psi

![Figure-7.22: Comparison of CO₂ emission concentrations for different blends at T = 500 °F & P = 300 psi](image-url)
T = 500 °F & P = 350 psi

![Figure 7.23](image1)

Figure-7.23: Comparison of CO₂ emission concentrations for different blends at T = 500 °F & P = 350 psi

T = 550 °F & P = 300 psi

![Figure 7.24](image2)

Figure-7.24: Comparison of CO₂ emission concentrations for different blends at T = 550 °F & P = 300 psi
Figure-7.25: Comparison of CO₂ emission concentrations for different blends at T = 550 °F & P = 350 psi

CO₂ from the above results was observed to be on an increasing trend. Under higher temperatures and lower pressures, ULSD and B10 showed low CO₂ emissions, whereas B5 and B50 showed lower emissions under higher temperature and pressure conditions. B20 compared to the other blends showed low emissions for high temperatures and low pressures. Under lower temperatures and varying pressures, ULSD showed lesser emissions compared to the biodiesel. Under lower temperatures and higher pressures, an increasing trend in CO₂ was observed.

7.1.2 Temperature and Pressure Effects on Emissions

In this section, the concentrations of a blend at different temperature conditions keeping the pressure constant were compared. From the graphs, the effects of temperatures on the different blends were compared.
Figure-7.26: Comparison of variation in different gas component emissions for ULSD at constant pressure and varying temperatures

From the Figure-7.26, it was observed that as the temperature increased H₂ emissions decreased for the ULSD. CO emissions were high at lower temperatures indicating a decrease in the CO₂ emission concentration change. CO emissions are inversely proportional to CO₂, since, CO emissions indicate the amount of combustions the blend has obtained. Since, high CO was observed at lower temperatures lower CO₂ was observed and vice-versa. A decrease in N₂ emissions were observed as the temperature was increased. CH₄ was approximately the same at both the temperatures indicating no effect of the temperatures in the emissions. CO₂ emissions were not affected much by higher temperatures and pressures.
Figure-7.27: Comparison of variation in different gas component emissions for ULSD at constant pressure and varying temperatures

In the above condition, again H₂ emissions were observed to decrease as the temperature increased. CO emissions increased as the temperature increased under higher pressures indicating that the emission reduced at higher temperatures and lower pressures. CO₂ was observed to decrease since the increase in CO emissions under the tested condition. Not much effect was observed due to temperature change for N₂ and CH₄ under high pressures.
From Figure 7.28, it was observed that as the temperature increased $H_2$ emissions decreased. A decrease in CO emissions was observed as the temperature increased which produced an inversely proportionate $CO_2$ increase. It was incurred from the above results that, B5 was better combusted at higher temperatures and lower pressures.
Figure-7.29: Comparison of variation in different gas component emissions for B5 at constant pressure and varying temperatures

B5 emissions were very interesting. At low pressure, temperature didn’t matter too much. But, at high pressure, high temperature the emissions were high except for CO₂ which produced lower emissions. Again, it was observed that CO emissions were inversely proportionate to the emissions of CO₂. CH₄ was not affected much at any temperature or pressure change.
For B10, the emissions of all the components studied were very high as the temperature increased under lower pressures. In other words, for B10 temperature effects on the emissions were significant when the pressure was low. Very high concentration of CO indicated incomplete combustion. H₂ emission was observed to be very high under higher temperature and lesser pressure condition.
Figure-7.31: Comparison of variation in different gas component emissions for B10 at constant pressure and varying temperatures

The emissions reduced for B10 under higher pressures and varying temperatures. At higher pressures, not much concentration variation was observed. CO emissions were lesser compared to under reduced pressures and also increase in CO$_2$ indicates that the blend was better combusted. So, for B10 when the pressure is high, temperature doesn’t affect the emissions.
Figure-7.32: Comparison of variation in different gas component emissions for B20 at constant pressure and varying temperatures

The emissions decreased as the temperature increased under lower pressures. CO decrease and increase in CO₂ emissions indicated the combustion level attained by the blend at the different conditions. H₂ emissions very observed to be reduced as the temperature was increasing. So, for B20, temperature effects on the emissions were not as significant as pressure. Higher pressure is preferred for low emissions from B20 regardless of temperature.
The emissions of B20 reduced at higher pressures and varying temperatures. A decrease in CO emissions and increase in CO₂ suggested better combustion as the temperature increased under high pressures. Not much variation was observed for CH₄ and N₂. At high pressures temperature change did not affect the emissions much.
Figure-7.34: Comparison of variation in different gas component emissions for B50 at constant pressure and varying temperatures

Higher emissions were observed as the pressure decreased compared to the data at 350 psi. A decrease in CO emissions and increase in CO$_2$ suggested better combustion. Not much effect in emissions was observed for the components but N$_2$ and CH$_4$ showed high emissions as the temperatures were increased.
Reduced emissions were observed under lower pressures and lower temperatures. Increased CO indicated decreased CO$_2$. Again, not much variation was observed for the components except for N$_2$ and CH$_4$. It was observed that when B50 was being experimented high increase in temperatures were observed. This may be due to high release of heat from the blend.

**7.1.3 Pressure Effect:**

In this section, comparison was done based on how the concentrations have varied for different temperatures and pressures for each blend.
In Figure 7.36, how the pressures have affected the emissions were observed. From this graph it was incurred that decreased pressures showed high concentration variations under different temperatures. This graph also shows the concentration change under a constant pressure and varying temperatures. High concentration changes were observed under lower pressures for ULSD compared to higher pressures.
In Figure-7.37, how the concentrations have varied for different components under different pressures was observed. Not much variation was observed for CH₄ and CO₂ compared to H₂, CO, and N₂. Indicating that the temperature variation under a pressure did not affect the change in concentration for CH₄ and CO₂ much and H₂, CO, and N₂ showed acceptable change in the concentrations. Increased pressures increased the change in concentrations for B5.
Figure-7.38: Comparison of concentration variation in different gas component emissions for B10 at different temperatures based on pressure.

From Figure-7.38, it was seen that at lower pressures high concentration variations were observed at different temperatures for B10. It was inferred from the above graph that, at higher pressure not much change was observed from B10 emissions for higher pressures. Also comparing to B5, much less emissions were observed for B10 at high pressures.
A varying trend when B20 was tested under different pressures was observed. The concentration changes for H₂ and CO₂ were very high when B20 was burnt under lower pressures. N₂ and CH₄ did not show many changes in the concentrations. Again, CO showed some variation under higher pressures.
Figure-7.40: Comparison of concentration variation in different gas component emissions for B50 at different temperatures based on pressure

From the above graph, a considerable change in concentration levels under low pressures was observed. CO₂ and N₂ showed high changes in the concentration levels when tested under lower pressures. CH₄, CO, and H₂ showed very less change in the emissions at varying pressures. It was observed that, N₂ and CO₂ contents decreased at higher pressure as the biodiesel blending increased from B5 to B50.

7.1.4 Percentage Component in Blend:

In this section, a graph was plotted with the percentage of each component concentration each blend has produced at a particular temperature and pressure.
**T = 500 °F & P = 300 psi:**

![Graph showing percentage of each gas component emissions in different blends at 500 °F and 300 psi.](image)

**Figure-7.41:** Comparison of percentage of each gas component emissions in different blends at T = 500 °F & P = 300 psi

CO₂ emission increased as biodiesel content increased. So, ULSD CO₂ composition was lowest and for B50, CO₂ was highest. Also, N₂ and CH₄ were not affected much by blend variation. CO was the least observed for B20 which was inversely proportional to the CO₂ produced by B20 than any other blend. The graph shows that B20 combustion was better at this temperature and pressure combination than the other blends.
In this scenario, interestingly CO\textsubscript{2} emissions were high for all the blends. B5 and B10 had higher CO emissions indicating that greater combustion was possible. H\textsubscript{2} emissions were very low for B5 and B50 compared to the other blends. N\textsubscript{2} for B5 was observed to be very low compared to the other blends. CH\textsubscript{4} and N\textsubscript{2} did not show much variation other than for B5.
As the temperature increased, B50 produced very high CO$_2$ and N$_2$ compared to the other blends. However, CO production was the lowest. Hydrogen produced was lower for B50 compared to the other blends. CH$_4$ and N$_2$ were approximately the same for all the blends. CO was observed to be high for B10 compared to the blends.
At higher temperatures, B50 produced higher N\textsubscript{2} emissions. CO emissions were very high for B5 and B10. B20 produced high CO\textsubscript{2} emissions and least CO emissions. H\textsubscript{2} emissions were the least for B50.

### 7.1.5 Emissions in Each Blend

In this section, the percentage of each component present in each blend at different temperatures and pressures was identified.
In Figure-7.45, the components were tested keeping the pressure constant. It was observed that, CO emissions were greater under lower temperatures and pressures and high CO₂ emissions for high temperatures and lower pressures which may indicate that at higher temperatures and pressures ULSD reached better combustion. Also, reduced levels of H₂ and N₂ emissions for higher temperatures were observed.
Figure-7.46: Comparison of percentage of each gas component emissions in ULSD keeping pressure constant and varying temperature

In Figure-7.46, the pressure was increased and the changes in percentage of each component concentration that may have occurred in the blend were observed. An increase in CO emissions was observed as the temperatures were increased at higher pressures and a decrease in CO\textsubscript{2} emissions. H\textsubscript{2} emission was also found to decrease. CH\textsubscript{4} and N\textsubscript{2} were observed not to be effected much by the increase in temperatures at higher pressures. ULSD was not affected much at higher pressures and varying temperatures.
Figure-7.47: Comparison of percentage of each gas component emissions in B5 keeping pressure constant and varying temperature

From Figure-7.47, it was observed that the temperature change did not affect the concentrations at lower pressures. It was observed that, CO and CO₂ concentrations increased as the temperature increased under lower pressures. H₂ and N₂ were observed to decrease as the temperature increased.
It was observed from Figure-7.48 that, as the pressures increased the CO$_2$ emissions increased. As the temperature increased CO$_2$ emissions decreased under high pressures. H$_2$ and N$_2$ emissions increased. Not much variation was observed at higher pressures but it was observed to decrease. CH$_4$ was observed to decrease as the temperature increased.
In the scenario, 300 psi and varying temperatures decrease in CO and CH$_4$ as the temperature increased under lower pressures was observed. Not much variation in CO$_2$ and N$_2$ emissions were observed under the conditions. Interestingly, H$_2$ was found to increase very much as the temperature increased.

Under pressures 350 psi and varying temperature conditions, as the temperature increased under high pressures an increase in CO was observed. CO$_2$ was observed to decrease as we reached higher temperatures. Not much change was observed for H$_2$, CH$_4$, and N$_2$. 

Figure-7.49: Comparison of percentage of each gas component emissions in B10 keeping pressure constant and varying temperature
Figure-7.50: Comparison of percentage of each gas component emissions in B10 keeping pressure constant and varying temperature

**B20**

Figure-7.51: Comparison of percentage of each gas component emissions in B20 keeping pressure constant and varying temperature
CO₂, H₂ were observed to decrease as higher temperatures were reached under lower pressures. CO, N₂, and CH₄ were observed to increase as temperature increase. This indicates that B20 reached better combustion under lower temperatures and pressures.

![Figure-7.52: Comparison of percentage of each gas component emissions in B20 keeping pressure constant and varying temperature](image)

H₂ and CO₂ were observed to increase as the temperature increased under higher pressures. CO decrease as temperatures reached high indicating that better combustion was attained at higher temperatures under higher pressures. Not much variation was observed for N₂ and CH₄.
Figure-7.53: Comparison of percentage of each gas component emissions in B50 keeping pressure constant and varying temperature

As the temperature increased, it was observed that CO\textsubscript{2} emissions increased and CO emissions decreased indicating better combustion. N\textsubscript{2} emissions were observed to increase as higher temperatures were reached. CH\textsubscript{4} emissions decreased and a considerable change was observed in the emissions for H\textsubscript{2} at higher temperatures under lower pressures.
Interestingly, at higher pressures a decrease in the emissions of CO$_2$ was observed. Effect of the pressure on CO$_2$ for B50 was very high. Very high increase in N$_2$ emissions as higher temperatures and pressures were reached. Not much variation was observed for H$_2$, CH$_4$, and CO under high pressures and temperatures.

Biodiesel is a carbon neutral source (Dowaki et al., 2007) and hence carbon compound on the whole were observed to be on the higher for biodiesel compared to ULSD. It was observed from the results that, the blends had different emissions at different pressures and temperatures. The emissions are based on the combustion level the blend had obtained at the given conditions. Some of the blends indicated very high emissions of CO and low emissions of H$_2$. The relationship between CO, CO$_2$, and H$_2$ was that whenever the HC has completely combusted, the hydrogen and carbon get separated and carbon

Figure-7.54: Comparison of percentage of each gas component emissions in B50 keeping pressure constant and varying temperature
combines with oxygen to form CO, CO₂, and very little Hydrogen and vice-versa. CH₄ was observed to be approximately same for all the blends on an average.

7.2 Scanning Electron Microscope

PM is one of the most dangerous emissions. It was observed that, PM with smaller particles is the most dangerous because of its longer residence time in the atmospheric suspension (Kittelson et al., 1998), higher specific surface and higher capability to penetrate into the respiratory system (EPA, 2002; Munack et al., 2006; Lue et al., 2001), and lower filterability in traps and filters (Jung et al., 2006; Kittelson et al., 1998). In this section, morphological data of the PM for the blends were identified. It is difficult to evaluate the effect of biodiesel on the particle size distribution because these are very sensitive to the dilution needed prior to the sampling and to the engine operating conditions (EPA, 2006; Armas et al., 2007).

The flue gases from the emissions of the fuel burnt were passed through the PTFE filter papers and then sent to the GC for gas analysis. Particulate matter generated during the combustion of each blend was expected to be collected on the filter papers. In order to identify the morphological characteristics of the particulate matter, the filter papers were studied using scanning electron microscope FEI Quanta 3D FEG. FIB-SEM instrument is equipped with a number of high-resolution imaging and surface analysis methodologies, such as low vacuum backscatter electron imaging (BSE), secondary electron (SE) imaging, and ion induced secondary imaging (ISE) and energy dispersive x-ray detector (EDS) (Instrument manual, FEI).
The filter paper was sputter coated with 0.5” nm palladium-gold plating before placing inside the instrument. Figures in the tables show few particles observed under scanning electron microscope for blends B5, B10 & B50. The morphological characteristics of the observed particles were analyzed using ImageJ (Tiago and Rasband, 2010). ImageJ was developed by National Institutes of Health (NIH). With this software observed particles were analyzed for the area and perimeter of the particulates. The shape factors were then calculated using the equation (Shandilya and Kumar, 2010).

\[ S_f = \frac{4\pi A}{P^2} \]

where, A is the particle area and P is the particle perimeter.

Tables-7.4 & 7.5 shows the images of particulate matter for different blends with their shape factor, shape, area, perimeter, and diameter:

**B5**

**Table-7.4: Images obtained from SEM for B5 Blend**

<table>
<thead>
<tr>
<th>Image</th>
<th>Shape factor</th>
<th>Shape</th>
<th>Area (micro-meter^2)</th>
<th>Diameter (micro-meter)</th>
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</thead>
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<td>35.5</td>
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<td>Height</td>
<td></td>
</tr>
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</tr>
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<td>38.2</td>
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<td>Oblong</td>
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</tr>
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<td></td>
<td>Shape</td>
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<td>Height</td>
<td>Angle</td>
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<td>775.0</td>
<td>34.3</td>
</tr>
<tr>
<td>Top right image</td>
<td>0.70</td>
<td>Pentagon</td>
<td>525.0</td>
<td>32.4</td>
</tr>
<tr>
<td>Bottom left</td>
<td>0.50</td>
<td>Rectangle</td>
<td>369.9</td>
<td>35.5</td>
</tr>
<tr>
<td>Bottom right</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table-7.5: Images obtained from SEM for B10 Blend

<table>
<thead>
<tr>
<th>Image</th>
<th>Shape factor</th>
<th>Shape</th>
<th>Area (micro-meter²)</th>
<th>Diameter (micro-meter)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td>0.46</td>
<td>Rectangle</td>
<td>2292.1</td>
<td>83.2</td>
</tr>
<tr>
<td><img src="image2.png" alt="Image" /></td>
<td>0.71</td>
<td>Square</td>
<td>921.6</td>
<td>41.3</td>
</tr>
<tr>
<td><img src="image3.png" alt="Image" /></td>
<td>0.82</td>
<td>Pentagon</td>
<td>4164.7</td>
<td>84.5</td>
</tr>
<tr>
<td>Shape</td>
<td>Area</td>
<td>Perimeter</td>
<td>Ratio</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>--------</td>
<td>-----------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>Square</td>
<td>0.58</td>
<td>352993</td>
<td>2546</td>
<td></td>
</tr>
<tr>
<td>Square</td>
<td>0.49</td>
<td>2711.7</td>
<td>82.2</td>
<td></td>
</tr>
<tr>
<td>Pentagon</td>
<td>0.76</td>
<td>564.2</td>
<td>36.7</td>
<td></td>
</tr>
<tr>
<td>Image</td>
<td>Area (sq cm)</td>
<td>Perimeter (cm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>--------------</td>
<td>----------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rectangle</td>
<td>4842.3</td>
<td>122.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agglomerate</td>
<td>596.3</td>
<td>34.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentagon</td>
<td>3268.9</td>
<td>77.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### B50:

Table-7.6: Images obtained from SEM for B50 Blend

<table>
<thead>
<tr>
<th>Image</th>
<th>Shape factor</th>
<th>Shape</th>
<th>Area (micro-meter^2)</th>
<th>Diameter (micro-meter)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.69</td>
<td>Sphere</td>
<td>465.9</td>
<td>31.1</td>
</tr>
<tr>
<td>Shape</td>
<td>Area (mm²)</td>
<td>Perimeter (mm)</td>
<td>Ratio</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
<td>----------------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>Square</td>
<td>246.8</td>
<td>23.6</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>Oblong</td>
<td>106.3</td>
<td>14.5</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>Pentagon</td>
<td>1925.2</td>
<td>64.6</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>Shape</td>
<td>Area</td>
<td>Perimeter</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
<td>-----------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triangle</td>
<td>0.49</td>
<td>2317.2</td>
<td>100.8</td>
<td></td>
</tr>
<tr>
<td>Oblong</td>
<td>0.42</td>
<td>14602.3</td>
<td>199.7</td>
<td></td>
</tr>
<tr>
<td>Rectangle</td>
<td>0.67</td>
<td>398.3</td>
<td>34.5</td>
<td></td>
</tr>
</tbody>
</table>
B5:

Figure-7.55: Graph representing shape factor vs. particle for B5

Based on the above particulate matter images we have observed that:

- Most of the particulate matter observed was pentagons.
- The area ranged between 370 square micrometer to 5499 square micrometer^2.
- Shape factor for B5 was observed to be in the ranges from 0.25 to 0.86.
Based on the above particulate matter images, we observed that:

- Most of the particulate matter was square shaped.
- The area of the particulate matter ranged between 564.2 square micrometer to 3529931 square micrometer.
- The shape factor ranged from 0.29 to 0.82.
From the above particulate images for B50 it was observed that:

- Most of the particulate matter observed was square and oblong.
- The area of the particulate matter ranged from 106.3 square micrometer to 14602.3 square micrometer.
- The shape factors ranged from 0.42 to 0.69.

The SEM results from the literature review show that the combustion of particles produce less than 50nm (Tsolakis et al., 2006; Marthis et al., 2005; Munack et al., 2005; Jung et al., 2006; Munack et al., 2006; Schroder et al., 2001). However, our results showed very high particle matter size range. It appears that our filter papers have been contaminated with the ambient air. Therefore, the experiments should be repeated. The above SEM results should not be used.
Chapter 8

Conclusion and Future Work:

8.1 Conclusions

- From the graphs discussed in the previous section, it can be incurred that H\textsubscript{2} emissions have decreased as the biodiesel blend increased. But at higher temperatures and lower pressures H\textsubscript{2} showed a varying trend. The emissions of H\textsubscript{2} were found be higher under lower temperatures and pressures.

- High CO emission indicates incomplete combustion. CO was observed to increase as the blend increased. CO emissions were observed to be more influenced by the temperature than pressure. The emissions were comparatively lower under low temperatures compared to the high temperatures.

- N\textsubscript{2} showed an increasing trend for higher biodiesel contents. It appears that pressures did not affect the N\textsubscript{2} emissions under low temperatures whereas under high temperatures, high pressure played a significant role on the emissions of biodiesel.
• Not much variation was observed for CH$_4$ for the blends under the tested conditions.

• The CO$_2$ emission from the results was observed to be on an increasing trend as the biodiesel blending was increasing except for B20. Under higher pressures and temperatures CO$_2$ emissions were comparatively lower for all the blends except for B20.

• ULSD showed lower emissions under low temperatures and varying pressures compared to biodiesel. High concentration changes were observed under lower pressures for ULSD.

• B5 showed lower emissions under lower temperatures and higher pressures. High concentration changes for observed under higher pressures.

• B10 showed the least emissions under lower temperatures and lower pressures. Higher concentration changes were observed under lower pressures.

• B20 showed lower emissions under high pressures and varying temperatures. Higher concentration was observed under lower pressures.

• B50 showed the least emissions under lower temperatures and higher pressures except for CO$_2$ which showed lower emissions under higher temperatures and pressures. Under lower pressures B50 concentrations were higher.

• For low H$_2$ emissions, B5 combustion under low temperatures and high pressures is preferred.

• For low CO emissions, B20 combustion under high temperatures and pressures is preferred.
• For low $N_2$ emissions, B5 combustion under low temperatures and high pressures is preferred.

• For low $CH_4$ emissions, B5 combustion under low temperatures and high pressures is preferred.

• For low $CO_2$ emissions, ULSD combustion under low temperatures and low pressures is preferred.

8.2 Future Work & Recommendations:

• A detailed study on the particulate matter should be done. The relationship between particle morphology and engine conditions needs to be investigated.

• We have tested the biodiesel blends made from soy bean. Different feedstock’s of biodiesel should be tested for emissions.

• We have tested biodiesel for blends B5, B10, and B50 and compared to the results of ULSD and B20, more biodiesel blends should be tested.

• Different temperature and pressure combinations can be tried out as some blends produced lower emissions under lower combinations and some at higher and varying combinations.
References


48. Intermodal Transportation Institute, Final Report (summary) Toledo Area Regional Transit Authority (TARTA) and the City of Toledo Biodiesel Study; 2006 – 2009, The University of Toledo, 2010.


66. **National Institutes of Health,** NIH is one of the world's foremost medical research centers, a part of the U.S. Department of Health and Human Services.


77. **Krahl, J., Munack, A., Schro¨ der, O., Stein, H., Herbst, L., & Kaufmann, A. (2005).** Fuel design as constructional element with the example of biogenic and fossil


Accessed on April, 2010.
Appendix:

GC Graphs:

Below are the graphs obtained from Gas Chromatography.

**Temperature @ 500F and Pressure range @ 300psi**

B5

Figure-A1: Intensity vs. time for B5 at T = 500F and P = 300psi
Figure-A2: Intensity vs. time for B10 at T = 500F and P = 300psi

Figure-A3: Intensity vs. time for B50 at T = 500F and P = 300psi
Comparing to B20 and ULSD

B20

Figure A4: Intensity vs. time for B20 at $T = 500\text{F}$ and $P = 300\text{psi}$

ULSD

Figure A5: Intensity vs. time for ULSD at $T = 500\text{F}$ and $P = 300\text{psi}$

111
Temperature @ 500F and Pressure range @ 350psi

B5

Figure A6: Intensity vs. time for B5 at T = 500F and P = 350psi

B10

Figure A7: Intensity vs. time for B10 at T = 500F and P = 350psi
Figure-A8: Intensity vs. time for B50 at T = 500°F and P = 350psi

Compared to B20 and ULSD

B20

Figure-A9: Intensity vs. time for B20 at T = 500°F and P = 350psi
Figure-A10: Intensity vs. time for ULSD at T = 500F and P = 350psi

Temperature @ 550F and Pressure range @ 300psi

B5

Figure-A11: Intensity vs. time for B5 at T = 550F and P = 300psi
Figure-A12: Intensity vs. time for B10 at T = 550F and P = 300psi

Figure-A13: Intensity vs. time for B50 at T = 550F and P = 300psi
Compared to B20 and ULSD

B20

Figure A14: Intensity vs. time for B20 at T = 550F and P = 300psi

ULSD

Figure A15: Intensity vs. time for ULSD at T = 550F and P = 300psi
Temperature @ 550F and Pressure range @ 350psi

B5

Figure-A15: Intensity vs. time for B5 at T = 550F and P = 350psi

B10

Figure-A16: Intensity vs. time for B10 at T = 550F and P = 350psi
Figure-A17: Intensity vs. time for B50 at T = 550F and P = 350psi

Compared to B20 and ULSD

Figure-A18: Intensity vs. time for B20 at T = 550F and P = 350psi
Figure-A19: Intensity vs. time for ULSD at $T = 550^\circ$F and $P = 350$psi
Experimental Setup Pictures

Below are the equipments used and the experimental setup.

![Experimental setup](image1)

**Figure-A20: Experimental setup**

**GC setup:**

![GC setup](image2)

**Figure-A21: GC setup**
Batch reactor setup:

![Batch reactor setup](image)

**Figure-A22: Batch reactor setup**

Filter paper casing:

![Filter paper casing](image)

**Figure-A23: PTFE filter paper casing**
FEI Quanta 3D FEG, SEM apparatus:

Figure-A24: FEI - SEM analyzer
Figure-A25: FEI - SEM analyzer

Sputter coater:

Figure-A-26: Sputter coater
Figure-A27: Sputter coater

Figure-A28: Sputter coater