

**Lubricant Oil Consumption Effects on Diesel Exhaust Ash Emissions Using a Sulfur Dioxide Tracer Technique and Thermogravimetry**

by

Michael J. Plumley

B.S., Mechanical Engineering  
U.S. Coast Guard Academy, 1998

Submitted to the Departments of Ocean Engineering and Mechanical Engineering in Partial Fulfillment of the Requirements for the Degrees of

Master of Science in Naval Architecture and Marine Engineering  
and  
Master of Science in Mechanical Engineering

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May 2005

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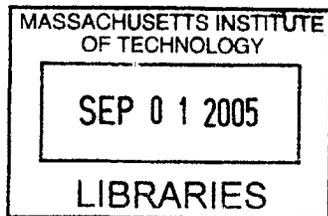
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## **ABSTRACT**

A detailed experimental study was conducted targeting lubricant consumption effects on diesel exhaust ash levels using a model year 2002 5.9L diesel engine, high and low Sulfur commercial lubricants, and clean diesel fuels. Regulatory decreases in allowable particulate matter emissions for on road diesel engines are driving industry to develop diesel particulate filters to trap and combust particulate. Remaining ash not combusted in this process clogs filters requiring engine down time and additional cleaning expenses. Recent reductions in fuel Sulfur and ash levels have also made lubricant consumption a significant relative contributor to particulate and ash generation. The goal of this study, a detailed understanding of lubricant contribution to particulate formation and ash transport, is required to enhance future filter design. The use of ultra clean fuels enhances accuracy of the Sulfur Dioxide tracer technique for estimating lubricant consumption and increases the relative contribution of lubricant to particulate emission. Results indicate the subject engine lubricant consumption is typical of others reported in literature. Particulate matter emission increases were measured after switching from a relatively low Sulfur, low sulfated ash oil to a high Sulfur, high sulfated ash lubricant. Volatile organic fraction and ash emission rates measured using thermogravimetric analysis indicate exhaust ash increases correlate with increasing sulfated ash content and lubricant consumption. Increased exhaust Sulfur and wear metal debris can also increase relative ash in particulate. Particulate generated using high Sulfur fuels has a higher ash emission rate than that obtained using near zero Sulfur fuel.

The consequences of on road emissions improvements will have a significant impact on the marine industry in coming years. New emissions regulations are reducing allowable particulate emission from marine diesels for the first time, with adaptation of on road technologies for these applications expected in the near future.

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# CHAPTER 1 INTRODUCTION

## 1.1 Motivation

US and foreign emissions regulations require significant reductions in particulate matter (PM) and  $\text{NO}_x$  emissions from heavy duty diesel engines in 2007. It is widely regarded by industry that continued efforts to reduce PM using in engine technology are not viable. Manufacturers will begin installing diesel particulate filters to reduce PM emissions to required levels. These traps rely on regeneration techniques currently being developed to remove the PM from the filters. Any regeneration scheme will leave ash, the incombustible metallic matter left after regeneration has occurred. Accumulation of this ash causes trap plugging and increased backpressure on engine exhaust, requiring removal and cleaning of the filter. For this reason technological advances are required to increase cleaning intervals. Regulations reducing Sulfur levels in fuels and impending standards addressing oil Sulfur levels are just some of the measures being taken to further reduce ash emission. In order to effectively reduce levels understanding of the mass transfer of ash is necessary. With this information better regeneration techniques can be constructed and the relative impacts of engine and lubricant chemistry may be addressed.

This document is intended for the future researcher, particularly those working on the subject or similar test apparatus. During the course of this study those works in literature and in local lab documentation which provided detailed information on testing specifics, which are not normally found in published papers, were invaluable in duplicating conditions and comparing data. Likewise several hours were spent bringing equipment online whose documentation had been lost over time.

## 1.2 Emissions Requirements History

### 1.2.1 Particulate Matter Environmental Effects

Diesel particulate matter is a contributor to particle smog and acid rain. The submicron size of particulate provides considerable surface area for adsorption and condensation of various engine pollutants within the exhaust gas stream. The presence of polyaromatic hydrocarbons (PAH) and other volatile organic compounds have led to the identification of PM as a known

carcinogenic. Particulate of 10 micron and smaller,  $PM_{10}$ , is particularly dangerous to health due to its effects on the lungs.

### 1.2.2 $SO_x$ and $NO_x$ Environmental Effects

$NO_x$  is the primary contributor to photochemical smog and Ozone through reaction with sunlight, unburned hydrocarbons, and atmospheric Oxygen.  $NO_x$  was the last of major criteria pollutants to receive significant regulatory attention, hence ambient levels have not dropped in proportion to the rates of the other five criteria pollutants over the past 40 years[1].  $NO_x$ , along with  $SO_x$ , is also a contributor to acid rain.  $NO_2$  formation from NO occurs in the atmosphere, exhaust, and cylinder in various degrees.  $NO_2$  can react with  $H_2O$  in the upper atmosphere to form Nitric acid,  $HNO_3$ . Likewise  $SO_2$  formed in cylinder combustion reacts with local  $O_2$  to form  $SO_3$  and then with  $H_2O$  to form Sulfuric acid,  $H_2SO_4$  [1]. On their own  $NO_x$ ,  $SO_x$ , and  $O_3$  are oxidants and harmful to plant life[2].

### 1.2.3 Emissions Regulations

A complete history of the evolution of the Clean Air Act and enforcement of emissions regulations is beyond the scope of this work, however a summary is presented for context. The history of national environmental regulations concerning diesel emissions dates back to the passage of the Clean Air Act of 1963 which was amended in 1965 to add the Motor Vehicle Air Pollution Control Act. Additional amendments were made in 1966, 1967, and 1969 and required state establishment of regulations within air quality regions[3]. Failure of state enforcement led to the passage of a new and completely rewritten Clean Air Act of 1970 (CAA). This act set the National Air Quality Standards (NAAQS) and standards for emissions from motor vehicles [4]. The amendment of 1977 was enacted to set more realistic goals over the highly ambitious 1970 act. A drastic amendment was again made with the passage of the Clean Air Act of 1990 which set greater controls based on new technology and advocated the use of low Sulfur fuels [3]. Additional changes to regulation were made by the Environmental Protection Agency (EPA) in 1997, with future amendments currently being discussed [5].

With respect to the CAA the EPA is primarily concerned with six criteria pollutants. These include Ozone ( $O_3$ ), Particulate Matter (PM), Carbon Monoxide (CO), Nitrogen Oxides ( $NO_x$ ),

Sulfur Dioxide (SO<sub>2</sub>), and Lead (Pb)[6]. IAW the CAA the EPA has set regulations for different source classes. The breakdown is listed in table 1:

<b>On Road Vehicles</b>	<b>Non Road Vehicles, Engines, Equipment</b>
Light-duty vehicles	Non road gasoline, diesel, and 'other' equipment and vehicles
Light-duty trucks	Aircraft
Heavy-duty trucks	Marine Vessels
Medium duty passenger vehicles	Locomotives
Motorcycles	

**Table 1: Classification of Mobile Emissions Sources**

These sources are application specific and not equipment specific. For this reason a particular model engine may be required to meet different criteria depending on its use. The motivation for this study was driven by motor vehicle manufacturer efforts to meet EPA regulations aimed at the Heavy Duty Diesel Truck category, however the information is applicable to any diesel application from a fundamental standpoint, including smaller marine diesels which are generally considered under the non road diesel category.

### 1.3 Previous Oil Consumption Work and Theory

#### 1.3.1 Lubricant Properties, Purpose, and Classification

The history of lubricant technology and research could easily fill this entire volume. As engine technology has progressed through the years lubricant technology has evolved as an entire industry. As such engine manufacturers and lubricant companies often must work together to determine necessary requirements and industry needs. Regulatory requirements motivating this study are also driving industry discussions seeking to set the next API oil category, which is currently designated PC-10.

Lubricant stock generally comes from crude oil distillations in the 340-540°C boiling range placing them at the heavier end of the distillation curve compared to lighter fuels such as diesel, kerosene, gasoline, and LPG[7]. The remaining composition consists of additives, generally designed to meet the specific requirements of particular applications based on engine size, configuration, and use. Lubricants serve several functions within the engine, primarily reducing friction, protecting against corrosion and wear, sealing rings and liners, and controlling undesirable products[8].

Additives are varied and generally proprietary in nature. Most consist of metallic detergents and zinc dithiophosphate (ZDTP) to control unwanted deposits in the oil and engine wear. Detergents also control acid formations from sulfated fuel. These contribute to the overall sulfated ash content and are generally for durability enhancement in diesel engines[9]. Additional ashless additives may also exist such as oxidation inhibitors and dispersants. Metallics, and in addition Sulfur and Phosphorous, are particularly harmful to catalyst technology. Sulfated ash is a measure of the metallic composition of a lubricant which may include Calcium, Magnesium, Silicon, or Zinc. The actual sulfated ash percentage is generally higher than a simple summation of these component percentages as will be discussed later. Givens et al characterized the Sulfur sources in test oils in terms of bond strength: detergents with strong Sulfur bonds, base oils with strong S bonds, and ZDTP with lower strength Sulfur bonds. In these studies ZDTP contributed most if not all of the Sulfur to the after treatment system.

The use of biodegradable lubricants for diesel vehicles has been proposed in the form of vegetable oils given their lower Sulfur content and lack of polycyclic aromatic hydrocarbons[10].

Classification of oils in the United States is generally defined by SAE viscosity grades and API classifications, with manufacturers recommending those oils particularly well suited to their product. Emissions regulations increase the need for cooperation between engine manufacturers and lubricant and fuel companies with in engine technology no longer sufficient to guarantee restrictions can be met.

Government agencies have sought desulfurization of fuels while auto manufacturers haven increasingly become interested in the classification processes of lubricants. The next classification of oil, being developed under a program known as PC-10, will be influenced heavily by increasing 2007 and 2010 emissions restrictions and the requirements of after treatment technologies designed to meet them. In particular lubricant volatility, as well as Phosphorous, Sulfur, and ash contents will be the focus of limitations, with sulfated ash the driving factor[11]. This will be the first time API has set chemical limits, however these have been set by manufacturers using their own classifications for particular applications. These have generally required ash levels of 1.85%<sub>wt</sub> with the majority of API CI-4 commercial oils on the market today on the order of 1.50%<sub>wt</sub> sulfated ash. The following figure shows a collection of

sulfated ash levels reported in commercial oil specifications sheets for several CH-4 and CI-4 15W40 lubricants.

In Japan and the EU separate classification systems and emissions regulations exist. Japan has the highest NO<sub>x</sub> and PM restrictions and was the first to issue chemistry specific oil classifications, limiting heavy duty diesel sulfated ash content to below 1.1%<sub>wt</sub> in its DH-2 standard. Light duty vehicles have a much lower standard at .6%<sub>wt</sub>[9].

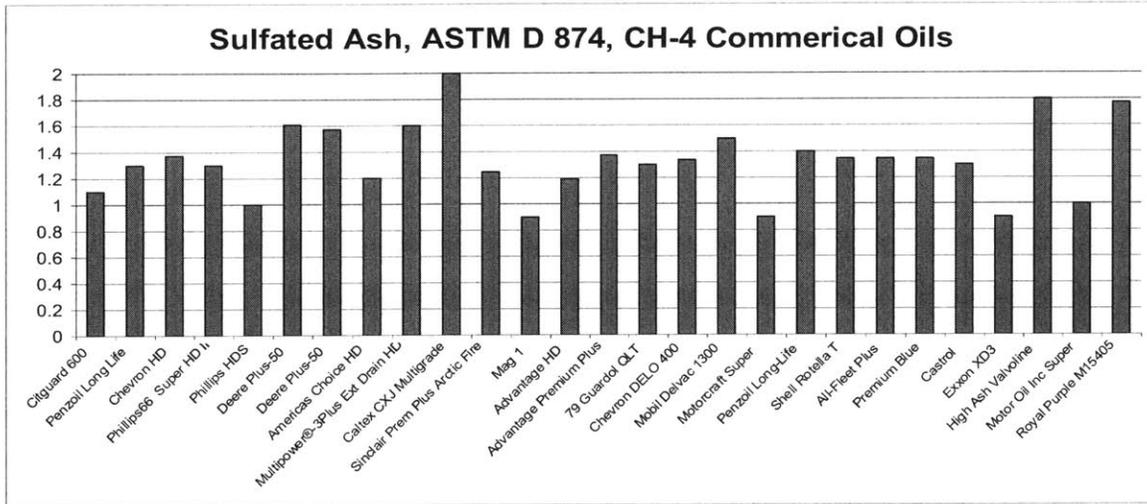


Figure 1 Sulfated Ash levels of various 15W40 CH-4 commercial lubricants

### 1.3.2 OC Sources and Mechanisms

Oil consumption has always been a concern of engine manufacturers and lubricant formulators for a variety of reasons. Recently consumption of lubricants has presented greater emissions concerns with oil derived pollutants approaching levels on the order of the fuel derived species given the application of cleaner fuels. Lubricant additives frequently contain material not present in fuel making them even more detrimental to overall emissions generation despite consumption on such a smaller scale. The presence of Sulfur in common oils is now of greater concern given its reduced presence in fuels. Escape of this Sulfur through the exhaust system from lube oil consumption can poison catalysts meant to treat non-sulfated exhaust. It can also increase Sulfur Dioxide emissions previously eliminated by the removal of Sulfur from fuels. While commercial oils generally do not contain sufficient Sulfur to produce excessive Sulfur Dioxide given current oil consumption rates in rare instances emissions can be significant as shown in the use of a commercial oil in this study. Since oils have significantly higher ash levels

small oxidation in cylinder can have the effect of adding ash to the after treatment system at a much higher rate than that of the same amount of fuel burned.

Several mechanisms of oil consumption exist. These mechanisms are influenced by a variety of controllable and uncontrollable factors. In general they include[12]:

- Transport into cylinder
- Blowby entrainment
- Evaporation in cylinder: influenced by piston-ring geometry and behavior, liner surface, cylinder bore geometry, temperature, oil properties including volatility, and operating conditions.

An additional source not usually included due to the ease of control is physical system leaks- generally attributed to system maintenance. Ideally these should be zero.

It is the symptoms of engine operating conditions, not the conditions themselves, which increase or decrease oil consumption. At higher speed and load piston ring behavior will affect degree of throw off and leakage of oil past the ring groove. Higher speed will also affect the degree of throw off given the acceleration of the piston. Higher loads generally increase liner temperatures leading to increased evaporation.

Oil properties can play a significant role in oil consumption. Increased oil volatility has been shown to reduce oil consumption, particularly as engine speed and load increase[12]. This is presumably due to liner temperature increasing influence on evaporation and throw off effects from the piston.

### 1.3.3 Measurement Techniques and Background

Several techniques for the measurement of oil consumption have been employed historically. Techniques can generally be divided into two categories: direct measure and tracer method. The first set includes gravimetric weighing methods as well as estimation based on volumetric changes, such as measuring sump level decreases. Gravimetric methods are reportedly accurate to within 10%[13, 14]. Tracer methods employ the monitoring of engine out emissions in the form of gas or particulate in search of trace chemicals either doped into the oil or already present as part of the designed composition. Tracers include Carbon-14[15], Tritium[13], metallics such as Calcium and Zinc[16-18] and Sulfur Dioxide[12, 19-24].

The SO<sub>2</sub> tracer method of oil consumption estimation is well documented and has been in practice since the 1970's, with the first application to diesel engines published in the 1980's. The SO<sub>2</sub> tracer technique has been compared in several studies to gravimetric results for verification of accuracy[23].

Examples of use of the technique include the work of Schofield and Yilmaz at MIT, the latter using the same Antek Sulfur Dioxide detector used for this study. The technique has gained further interest given the push towards lower Sulfur fuels and oils now that the presence of catalyst poisoning effects is known. The reduction of Sulfur in fuel has motivated development of extremely sensitive UV fluorescence analyzers [24]. Past SO<sub>2</sub> tracer work has overcome the limitations of SO<sub>2</sub> analyzers by doping the target oils with Sulfur. In this study a high Sulfur commercial oil was used, however its Sulfur content is much higher than that seen in common lubricants on the market. The direction of lubricant research will likely not produce such commercial candidates in the future given the Sulfur concerns stated previously. As such the Antek's 250 ppb<sub>v</sub> lower detection limit may adversely affect future studies aimed at systems with catalysts unless effective methods of detection at the devices lower limit are devised. Chapter 2 details several environmental variables which affect repeatability of the instrument and steps taken to minimize error to achieve better sensitivity. Most recently Pisano has developed a method using UV fluorescence capable of measuring in the <100 ppb<sub>v</sub> range and targeted at measuring undoped oils and fuels. This shows promise for the future of the SO<sub>2</sub> tracer technique in oil consumption study. Part per trillion lower detection limits are common amongst analyzers used for ambient conditions. The introduction of NO<sub>x</sub>, heat, and water vapor from exhaust gas constituents requires sample preparation which reduces sensitivity limits in automotive applications.

## 1.4 Previous Ash Emission Work and Theory

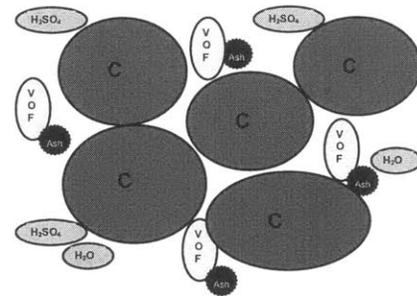
### 1.4.1 Particulate Matter Defined and Sources

A study of diesel ash cannot be carried out without a thorough understanding of soot and particulate matter. The specific details of soot formation and transport are still not fully understood and are therefore the subject of many ongoing studies. An excellent review of recent publications was presented by Stanmore et al[25]. Diesel particulate matter is strictly defined by the EPA under US 40CFR86 as matter collected on a fiber filter of given properties which has been diluted and cooled to 52°C. Particulate matter is often referred to by its more common and general title, soot. For the purposes of discussion in this paper particulate matter will be referred to when discussing the EPA's strict definition, and "soot" or "raw PM" will refer to particulate collected from the exhaust at temperatures above 52°C. This distinction is necessary given testing conditions used in this study which frequently did not meet the EPA's strict criteria by design. In addition, while particulate matter is defined as such, DPF do not collect all of the PM generated and are generally credited with capturing up to 90% of that produced by the engine.

US 40 CFR 86 details specific requirements for measurement of PM. These requirements are becoming more strict in the 2007 standard due to reduced levels of PM being generated by improved engine technology and increased knowledge of the test methods themselves. Specifically the PM generated is now at a level low enough to make the statistical noise generated by fluctuations in particulate collection filters and treatment devices significant. Chief among these noise factors are filtration size, material, temperature and humidity, with the actual weighing of filters providing the greatest source of error[26-28]. Chapter two details some of the concerns and uncertainties generated by different filtering media. A portion of this study was completed to confirm previous studies on filter effects.

Diesel particulate matter is composed of various elements yet is predominantly organic and elemental carbonaceous solid, ash, and Sulfur and water compounds. The volatile organic fraction (VOF) is generally attributed to unburned fuel and lubricant adsorbed on and condensed around the Carbon. Ash consists of metallics from lubricants, wear metal, and fuel additives and contaminants. Sulfur Dioxide, produced in the cylinder by fuel and lubricant species, combines with O<sub>2</sub> in the exhaust to form SO<sub>2</sub> and SO<sub>3</sub>. Additional reaction with water in the exhaust and later in the air forms Sulfuric acid which can condense and form on particulate.

Rich regions of the air fuel mixture within the cylinder produce solid Carbon agglomerates as well as small particles of atomized unburned fuel and lubricant oil which have evaporated. These unoxidized working fluids contribute to the Soluble (or as sometimes designated Volatile) Organic Fraction (SOF or VOF) in the exhaust and have traditionally been the focus of many studies due to their cancer causing properties. Diluted and cooled exhaust, such as that collected in EPA tests of particulate matter, contain diesel exhaust which has undergone cooling, condensing, nucleation, and adsorption converting the volatile matter into particulate. For this reason sampling at higher temperatures is more likely to leave volatiles in the gaseous phase and pass them through filters. In exhaust chemistries with high Sulfur content the condensing of Sulfuric acid can also lead to the formation of particulate matter separate from that adsorbed directly on Carbon. Hence collections of particulate matter are often heavier in terms of grams per unit time than a similarly collected higher heated raw PM sample.

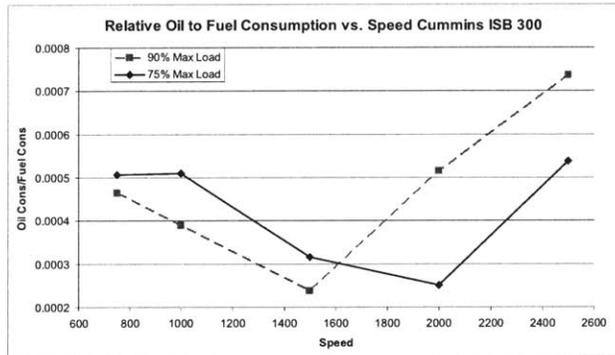


**Figure 2 Depiction of particulate matter composition**

Recent reductions in fuel Sulfur make oil contribution a matter of greater interest. Very high Sulfur in the lubricant can have effects on the order of those experienced by fuel when oil consumption is high. Hence oils are sometimes referred to by ‘equivalent fuel Sulfur’[29]. It should be noted that fuels containing higher Sulfur content also contain higher ash content. Recent studies suggest Sulfur is the leading cause of increased PM levels in high Sulfur versus low Sulfur fuels. Recent studies at MIT indicate reductions in fuel Sulfur correlate well to reductions in PM. Weight calculations also indicate Sulfur was not the sole cause of the changes in PM. While work on these fuel effects progresses data suggests changes in heat release properties between the fuels during combustion may also be a factor[30, 31].

Studies to determine the PM contribution from fuel and lubricant continue. Early studies suggested an increased percent contribution from lubricant at higher engine speeds[8]. This could be attributable to the relative increase in oil consumption vs fuel consumption over the speed range, however tests on the subject engine in this study do not indicate this trend as shown in the following figure. Increased oxidation of the charge mass and exhaust given higher cylinder and exhaust temperatures at higher speed and load could also influence this phenomenon given

fuel's higher volatility. This is related to the effect of oil viscosity and film thickness on particulate emission. Particulate emissions related to oils have been found to increase with decreasing viscosity (and the associated increase in volatility) whether it is related to oil chemistry or aging[32-34].



**Figure 3 Relative Oil to Fuel Consumption on MY02 Cummins 6 Cylinder ISB 300 Diesel. (Included in Appendix C)**

Studies in literature using 1995 standards showed oil derived particulates can account for as much as 25% of total allowable PM [35]. Similar findings are put forth in studies by Sharp et al[22].

Non ash PM may also be characterized as organic (OC) and elemental (EC) Carbon. Definition of these two components is also subject to variability based on measurement technique[36, 37]. As equivalence ratio increases for a given speed the relative concentration of EC to OC increases suggesting increases in fuel contribution and constant oil consumption. In addition particle size decreases. Studies using a Calcium tracer method have shown a correlation between increased OC and increased relative lube oil consumption[17].

#### 1.4.2 Ash Defined and Sources

Ash is a component of fuels and lubricants and as a result one of diesel PM and soot. Past studies have tended to focus on the measurement of EPA defined Particulate Matter (PM) emissions and standards are in place to ensure accurate and repeatable results. Diesel particulate filter regeneration challenges have raised the interest of the ash contribution of particulate matter considerably. Details of the complexities of defining and measuring ash are covered here and in chapter 2. In general it is composed of metallic additives in petroleum products used and engine wear particles.

The very definition of ash as it is related to diesel particulate filtering can itself be a lengthy academic exercise. The predominant sources of ash are noncombustible metallics in fuel and oil. Engine wear material and fuel and lubricant contamination can also contribute to ash as related to accumulation in DPF. For an effective working definition related to the problem of DPF clogging the author has chosen “that material left after a regeneration has occurred”. Given the difference in trap design and regeneration techniques the elemental composition of this “operational definition” of ash may vary from DPF to DPF. For purposes of discussion throughout this study this ash shall be referred to as “DPF ash”.

Several standards exist to define ash as it relates to the chemistry of fuel and oil. “Sulfated ash” is a standardized measure for lubricants and additives usually measured in accordance with ASTM 874 where it is defined as “the residue remaining after a specimen has been oxidized, and the residue subsequently treated with Sulfuric acid and heated to constant weight”. The measure of sulfated ash for organic materials, thereby including lubricants and fuels, by thermogravimetry is given by ASTM E2403 and defined as “the residue remaining after the sample has been carbonized, and the residue subsequently treated with Sulfuric acid and heated to constant weight”. These two methods differ primarily in the temperatures the material is raised to, the amount of material required for measurement, and the frequency of introduction of Sulfuric acid to the sample. The differences are primarily due to the test apparatus used with thermogravimetry employing a much smaller sample. Since ash mass will continue to decrease at elevated temperatures over long periods measures of composition can vary from lab to lab if specific standards are not agreed upon[38]. The addition of Sulfuric acid is added to account for

reaction of exhaust Sulfur with metallic particles within the tailpipe. This effectively increases the mass of measured ash contributed by metallic components through formation of sulfates[39].

Another standard, defining the measure of “ash from petroleum products” is given by ASTM D482 and is designed to characterize used fuels and lubricants. In this standard “ash forming materials” are defined as those “normally considered to be undesirable impurities or contaminants”. This looser definition is similar to that of D874 with igniting and heating of the sample to 775°C. The treatment and subsequent heating with Sulfuric acid is excluded.

A fourth method of estimation utilizing a simple summation of metallic components through elemental analysis has been proposed in some studies. Specifically Takeuchi compared two summation methods with those of ASTM standards[40]. The results differ from those obtained by the standards due to inter-element interferences produced during the combustion process[40, 41]. These variations require the specific definition of the standard of measurement used when making reference to a level of ash in a product.

Given these standard definitions there should still be a strong correlation between the sulfated ash level of the test fluids (oil and fuel) and the presence of DPF ash remaining in the filter. This correlation has been demonstrated in recent studies, however actual capture of ash calculated as a percentage of that expected based on complete combustion of oil and fuel consumed is generally around 30% -60% based on DPF studies. Nemoto et al showed a 30-50% capture rate of ash with 95% of the oil derived metals trapped[18]. Flow rate and temperature did not effect trapping rate and Calcium (Ca) was found to reside within the lubricant causing increases in sump concentration over time. Overall  $\text{CaSO}_4$  was still found to be the primary engine out ash component[18]. Givens et al found no relation between particle size and determined fluctuations in PM collected as a result of engine conditions had a greater effect than changing oil composition[13]. Correlation was found between sulfated ash composition of the oil and ash accumulation in the DPF, with 20-40% of the expected ash captured[13]. Studies have also suggested contributions from engine wear particles, and non combustible components present in ambient air and fuel contaminants, can contribute to significant ash emission. Kurihara et al found as much as 2-10% of accumulated ash was composed of metallic components not found in the lubricant and suspected of coming from engine wear[9]. During tests in our study PM containing easily observable engine wear particles contained approximately 10% higher ash levels as those samples without visible contamination.

It should be noted that DPF's do not trap all soot and PM and do not combust all of the non-ash raw PM. Significant ongoing research is targeted towards understanding the combustion properties of DPF's in terms of the effects of backpressure, PM loading, temperature of incoming exhaust, temperature distribution across the filter, catalyst influences, etc. A detailed discussion of all of these studies is beyond the scope of this work. The goal of this study is in an understanding of the lubricant contribution to these effects. The DPF does not collect all of the PM for two primary reasons. The first is trapping efficiency. Aerosol retention required by the EPA of filters used in studies of PM is higher than that of the ceramic filters commonly employed in DPF. This is for obvious backpressure reasons. The second reason is the cooling and condensation effects attributed to dilution tunnels required by the EPA in PM studies. DPF typically see exhaust gases at considerably higher temperatures than those seen at the end of a dilution tunnel. Hence volatiles condensed and captured by diluted PM tests are more likely to pass through DPF filters. To a lesser extent these gases will also pass through the filtration material used for PM tests if the sampled exhaust gas is not diluted.

#### 1.4.3 Measurement Techniques Investigated Previously

As stated ash measurement has gained increased interest in regards to engine design. Diesel particulate filter regeneration techniques vary from manufacturer to manufacturer. It is generally considered that an uncatalyzed trap will be regenerated by raising exhaust or trap temperature to approximately 600°C. Temperatures below this will lead to incomplete combustion of the particulate matter and temperatures above this will likely cause structural damage. Decreases in regeneration temperature are achievable using a catalyst upstream of the trap or in the fuel. Exhaust after treatments have not been used or studied in this work.

Past work in defining ash composition and contribution to total PM has generally been conducted using actual traps and sampling ash after regeneration or testing particulate matter in lab conditions after collection on filters. Analysis of particulate matter has largely focused on organic components due to their health effects and on particle agglomeration. Given the variety of compositional analysis techniques available in various laboratories several methods have been used. These methods include extraction techniques, spectrometry, and thermal techniques.

A popular method of PM analysis is the use of soxhlet extraction to characterize PM into soluble organic fraction (SOF) and non soluble organic fraction. Results from an MIT contracted

study using soxhlet extraction with subsequent Gas Chromatograph with Mass Selective Detector (GC/MS) analysis indicated this method is potentially effective if particulate filter loading exceeds .5 mg[42]. Results of that study, which incorporated sampling from a single cylinder experimental engine, varied considerably over the range tested due to light loading of filters. In samples where components of SOF were detectable the amount derived from lubricant was on the order of 90% vs. 10% from fuel. This percentage was stable over the range of conditions studied[42, 43]. These results suggest the SOF contributions are almost completely lubricant based, a conclusion consistent with similar studies in literature[22, 44, 45].

Several spectrometric methods have been used for characterization of PM and ash components including: Accelerator Mass Spectrometry (AMS)[15], X-ray Fluorescence (XRF)[16, 46], Aerosol Time of Flight Mass Spectrometry (ATOFMS)[17, 47], Inductively Coupled Mass Spectrometry[17, 47, 48], and X-ray Photoelectron Spectrometry[18].

In this study the use of Fourier Transform Infrared (FTIR) and Raman Spectrometry was considered as a possible method for characterization of particulate. Literature on this type of soot analysis is scarce given the greater applicability of the methods mentioned previously. FTIR is a common method for identification of soot and other contaminants in used oil, as well as for other organic chemical analysis[49]. FTIR is favorable for this type of study for several reasons, predominantly the ability to easily identify functional groups of hydrocarbons and the high absorbency of carbon and PM compared to other constituents within a well defined range of the infrared spectrum[50, 51]. The use of FTIR for characterization of PM on particulate filters was not found during a literature review.

Other methods for particulate characterization include X-ray diffraction (XRD) [9, 16, 18, 40]. Scanning Electron Microscopy (SEM)[16, 46], Energy Dispersive X-ray analysis (EDX)[16, 46], Inductively Coupled Plasma[13, 18, 40], and Scanning Mobility Particle Sizer (SMPS)[17, 30, 46, 52].

The most popular methods for thermal analysis of PM include thermogravimetric (TGA) and thermal optical techniques. The latter provide immediate information on the relative amounts of organic and elemental Carbon. Thermogravimetric methods have been used to determine ash composition of fuels, lubricants, and PM. Determination of volatile organic fraction using this method has been shown to correlate strongly with that found using soluble extraction methods discussed earlier, with VOF oxidation occurring between 150°C and 380°C[53-55]. VOF is

generally attributed to higher boiling point components of fuel and lubricants adsorbed onto particulates[56]. High exhaust temperatures in excess of 350°C may significantly reduce VOF contribution to particulate.

Several studies have been completed to characterize the regeneration characteristics as they occur inside the DPF. Fewer studies have been done to determine the oxidation effects of PM on much smaller filters in a thermogravimetric analyzer[57]. The heat transfer properties of these phenomena are not trivial and can also lead to significant differences in the amount of ash calculated due to charring and exothermal effects within the instrument[57].

Most studies seeking to measure DPF ash accumulation have focused on use of actual DPF with subsequent weighing after regeneration. Due to the lack of standardized regeneration techniques variability in those test methods could lead to variability in ash measured. For this reason published work must contain considerable information on temperature distributions and quantity of PM studied. In addition these methods can be time consuming. A goal of this study was the identification of a faster method to define the ash generating characteristics and mechanisms of different fuels, oils, and engine operating conditions. Some obvious disadvantages exist with this approach as well. It does not take into account different regeneration methods or the effect of large accumulation of ash and increased backpressure over time. Altering residence time with these factors can have a significant effect on PM and ash estimates[38].

## 1.5 Relation to Marine Emissions

### 1.5.1 Background

Marine emissions have recently come under greater scrutiny with the first significant federal regulations taking effect in the 1990's. The lag in marine emissions regulation is due to the relatively small number of engines affecting urban areas as well as the international coordination difficulties surrounding maritime law. Given the success of restrictions on land based sources marine emissions are contributing to greater percentages of overall pollutants. Some studies conducted over the past ten to twenty years have been aimed at estimating regional impacts[58, 59]. The California Air Resources Board (CARB) predicts within 20 years marine emissions may account for as much as 9% of NO<sub>x</sub> and 25% of PM on a statewide level[2]. Recent estimates suggest over 60% of this will come from large category 3 vessels[60]. A recent

review of Houston area marine related pollutants showed an increase in the average NO<sub>x</sub> output from 29.8 tons/day in 1993 to 31.5 tons/day in 1997[61].

In the US marine vessels are generally divided into three categories based on cylinder displacement and power:

**Table 2 Marine vessel emissions categories[62].**

Category	Displacement	Engine Type	Typical Power (kW)	General Use
1	<5 dm <sup>3</sup> , ≥37kW	Non-road diesel	500 to 8,000	tugboats, utility, fishing, and other commercial vessels in/around ports
2	5<dm <sup>3</sup> ≤0 dm <sup>3</sup>	Locomotive Engines	500 to 8,000	Similar to category 1
3	≥30 dm <sup>3</sup>	Large Marine Engines	2,500 - 70,000	container ships, oil tankers, bulk carriers, and cruise ships

For smaller marine engines there is considerable potential for the use of emissions technologies already developed for land based applications. Major engine manufacturers are currently working on employing on road technologies to marine applications, to include direct injection timing, exhaust gas recirculation (EGR), increased exhaust temperatures, and increased turbocharger efficiencies[2]. A considerable difference between on road and marine systems, particularly in smaller vessels, is the need to keep temperatures low below decks. This is crucial for fire prevention as well as crew tolerance and reduces the applicability of late injection strategies to reduce PM. Many marine exhaust systems are also cooled with incoming seawater. Such systems pose problems for the installation of catalysts or diesel particulate filters, with even ceramics susceptible to cracking due to rapid cooling from seawater. Exhaust cooling systems also transport particulate and its associated hydrocarbons directly into the water, particularly at higher loads in which lubricant consumption is a larger factor of emissions[33, 43]. Emissions solutions for category three vessels are further limited due to the use of residual fuels which contain considerably greater ash and Sulfur levels[62].

In addition to engine solutions non road diesel fuel Sulfur levels, limited to 500 ppm<sub>w</sub> in 2007 and 15 ppm<sub>w</sub> in 2012 will allow for greater use of current technologies including catalysts. These rules will not affect many category 2 and most category 3 engines which use residual fuels, however recreational and category 1 vessels will see considerable improvements. Larger vessel emission concerns are leading to a continued push for lower Sulfur levels in heavier marine fuels[63].

Recreational and Category 1 and 2 vessels are of concern to coastal communities as they account for the greatest proportion of vessels which remain in the local area. While Category 3 vessels are much larger and account for a greater contribution of pollution worldwide they are all large oceangoing vessels and most are foreign flagged. Despite their smaller size the first two categories produce a significant portion of controllable emissions in coastal areas. They are expected to account for approximately 25% of Houston area marine emissions, and 40% of California statewide marine emissions, by 2007[2, 61].

### 1.5.2 Recent US Legislation

Small recreational marine engines under 37kW are governed under the standards for non-road engines in 40 CFR 89: “Emission Standards for New Non Road Engines—Large Industrial Spark-Ignition Engines, Recreational Marine Diesel Engines, and Recreational Vehicles”. This regulation was signed in 2002. Specifics of the requirement are listed in the following table.

**Table 3 Summary of 2002 US recreational vessel emissions standards**

<b>Displacement (dm<sup>3</sup>)</b>	<b>CO (g/kW hr)</b>	<b>NO<sub>x</sub> (g/kW hr)</b>	<b>PM (g/kW hr)</b>	<b>Year</b>
.5-.9	5	7.5	.4	2007
.9-1.2	5	7.2	.3	2006
1.2-2.5	5	7.2	.2	2006
2.5+	5	7.2	.2	2009

Category 1 and 2 vessels are now regulated under 40 CFR 89 as signed in November 1999. This section, entitled “Control of Emissions of Air Pollution from New CI Marine Engines at or above 37 kW” is similar to non-road land based diesel regulations. Category 1 and 2 regulations are listed below. Blue skies regulations are voluntary standards designed to allow manufacturers to claim higher degrees of environmental friendliness until 2010. These engines also include onboard generators and other engines providing hotel and auxiliary services.

Category 3 vessel regulations, adopted in 2003, are very similar to recently adopted International Marine Organization (IMO) standards and are covered under 40CFR9 in “Control of Emissions From New Marine Compression-Ignition Engines at or Above 30 Liters Per Cylinder”[62]. Category 3 emissions regulations are also being driven based on Annex VI to 1973 International Convention for the Prevention of Pollution from Ships ( MARPOL) which is

expected to take effect in 2005 for all member nations[2]. MARPOL VI will set a 4.5% (45000 ppm<sub>w</sub>) limit on fuel Sulfur. It will also set aside SO<sub>x</sub> emission control areas (SECAs), predominantly in Europe, in which Sulfur limits will be 1.5% (15000 ppm<sub>w</sub>). While actual Sulfur content information is not widely available for heavy marine residual fuel, ASTM standards currently limit Sulfur content to 5.0% for residual and 1.5-2% for distillate intermediate fuels[64].

**Table 4 Summary of US Category 1 and 2 vessel emissions standards.**

Displacement (dm <sup>3</sup> )	Category	CO (g/kW hr)	NO <sub>x</sub> (g/kW hr) [blue skies]	PM (g/kW hr) [blue skies]	Year
<.9, ≥37kW	1	5	7.5 [4.0]	.4 [.24]	2005
.9-1.2	1	5	7.2 [4.0]	.3 [.18]	2004
1.2-2.5	1	5	7.2 [4.0]	.2 [.12]	2004
2.5-5.0	1	5	7.2 [5.0]	.2 [.12]	2007
5.0-15	2	5	7.8 [5.0]	.27 [.16]	2007
15-20, <3.3MW	2	5	8.7 [5.2]	.5 [.30]	2007
15-20, ≥3.3MW	2	5	9.8 [5.9]	.5 [.30]	2007
20-25	2	5	9.8 [5.9]	.5 [.30]	2007
25-30	2	5	11 [6.6] <sup>1</sup>	.5 [.30]	2007

Overall information on marine vessel emissions is limited in comparison to studies conducted in the automobile industry. The US Coast Guard has conducted limited studies on its fleet, with the most comprehensive to date conducted in the mid 1990's in support of EPA research regarding regulations requirements. That study included Coast Guard vessels ranging from 41' small boats to 378' cutters.

To gain a perspective of scale and highlight the higher rates exhibited by typical marine sources the Coast Guard 41' UTB, a category one vessel, is comparable in size to the heavy duty land based diesel studied here. These vessels, designed in 1967, are still in service and have twin Cummins VT-903 inboard engines with a combined 470 KW (630 HP). The 1995 study, conducted on each engine of one UTB using typical No 2 diesel fuel, generated the following average values for NO<sub>x</sub> and SO<sub>2</sub>[58]. Unfortunately PM was not measured.

<sup>1</sup> Older engines will be grandfathered. Vessel retrofit projects are affected by the regulations, with the definition of "new vessel" expanded in 40 CFR 94.2 to include older vessels receiving modifications worth over 50% of their current value. Companies may enter a trading program and account for average emissions across product families, with these average caps set at a less stringent 1.2 g/kw-hr for PM and 14.6 g/kw-hr for NO<sub>x</sub> [1].

**Table 5 Emissions for USCG smallboat[58].**

<b>Power/Speed</b>	<b>NO<sub>x</sub> (g/kW-hr)</b>	<b>SO<sub>2</sub> (g/kW-hr)</b>
100%	6.59	1.06
75%	7.56	1.97
50%	10.13	2.82
25%	5.11	2.55

For the MY02 Cummins 5.9L 6 cylinder diesel studied here SO<sub>2</sub> levels were considerably lower, with a maximum value of .1 g/kW-hr measured using no Sulfur fuel and high Sulfur oil. NO<sub>x</sub> levels for the MY02 engine were also far lower, at less than 2 g/kW-hr at the steady state conditions identified above.

Results in the 1995 Coast Guard study for the 110' Island class coastal patrol boat did include PM data. Values varied from .3-.4 g/kW-hr for steady state conditions of 25%, 50%, 75%, and 100% speed and load, with PM emission of 2-3 g/kW-hr measured at no load idle conditions. Values for NO<sub>x</sub> were generally twice those given for the UTB. SO<sub>2</sub> values were approximately half of those listed for the UTB[58].

### 1.5.3 Military Readiness Exclusions

US Navy and Coast Guard vessels, which are not included under MARPOL regulations for participating states due to agreed upon military exclusions, are currently directed by Congress to meet 1978 MARPOL V requirements, suggesting MARPOL VI will also be applied. DOD and Coast Guard installations and assets are also included under all provisions of the Clean Air Act. DOD petitioned for exclusions from the Clean Air Act in the interest of military readiness[65]. 40 CFR 94.908 details the "National Security Exemption" which excludes, without specific request, vessels exhibiting features "ordinarily associated with military combat..." used by federal agencies for national defense purposes. DOD is also exempt from the Endangered Species Act, the Marine Mammal Act, and the Migratory Bird Treaty Act [66].

The US Coast Guard has traditionally met or exceeded emissions requirements in the interest of environmental stewardship. While many vessel classes do not exhibit obstacles to compliance unique challenges due exist for some assets which make the use of the exclusions attractive to policy makers. The Coast Guard's aging 140 foot icebreaking tug fleet recently came under review given the class' new role in homeland security missions during warm weather

months and the need for extensive upgrade given their lengthy time in service. Designed for high load operations the vessels' main propulsion engines exhibit poor emissions characteristics with high lube oil consumption and particulate matter and unburned hydrocarbon emission at the low load conditions typical of security patrol cruising. Upgrade to modern high speed low emission engines would unduly hinder the vessels' primary icebreaking mission. To meet these challenges Coast Guard engineers have opted to forgo reliance on the compliance exclusion and recommended maintaining the current power plant configuration while employing other technological solutions to reduce oil consumption and particulate generation[67]. Similar challenges will also accompany larger icebreaker retrofit schedules as well as future vessel allocations.

## CHAPTER 2 EXPERIMENTAL APPARATUS, LIMITATIONS, AND CALIBRATION

### 2.1 Engine

The test engine used was a close to production development engine supplied by Cummins. The MY02 ISB 300 is a 6 cylinder, turbocharged, cooled EGR, 5.9 liter direct injection diesel rated at 224 kW at 2500 RPM and 890 N-M at 1600 RPM. The engine is governed by an engine control module (ECM) to meet 2002 emissions standards and control the various advanced components of the engine including the cooled EGR system, variable geometry turbocharger, and common rail fuel injection system. Cummins provided their in-house CalTerm software to communicate to the ECM from the lab. The CalTerm software provided an excellent tool for troubleshooting and checking the effectiveness and accuracy of the data acquisition instrumentation attached separately to the engine. In addition it provides the capability to adjust engine parameters outside those restricted by alarms on test engines without proprietary software. The software was loaded to effectively meet the 300 HP rating using number 2 diesel fuel. The engine was initially set up in the lab by previous researchers for use in testing of the effects of different fuel blends on emissions. Therefore a great deal of information was available on the engine prior to the study[30, 52]. Fellow researcher Alexander Sappok contributed significantly to the smooth running of the test engine, most notably in administration of the CalTerm software and in assisting with troubleshooting various equipment.

The power train also consists of a Digalog AE 250 eddy current dynamometer. Torque is measured by a Maywood instruments U4000, 500 kg load cell by resisting rotation of the outer casing. The Digalog 1022A-STD controller maintains engine speed at a given load and vice

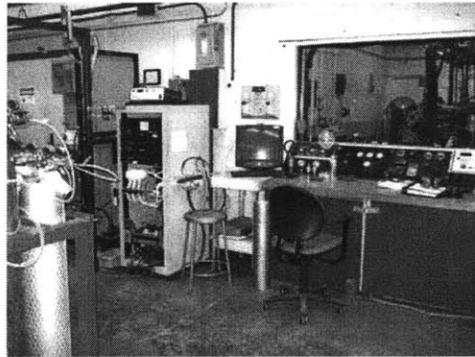


Figure 4 Lab configuration.

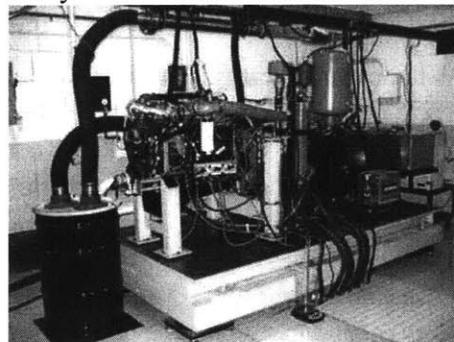


Figure 5 Cummins ISB300 on test bed.

versa. The controller and dynamometer were calibrated by previous researchers at two points, 50% and 100% load.

## 2.2 Data Acquisition Overview

### 2.2.1 Hardware

Initial data acquisition hardware was designed and installed by previous researchers [30, 52]. The engine is fully instrumented with thermocouples, pressure transducers, and flow meters to provide for extremely detailed monitoring and capture of engine conditions. In addition emissions and ambient condition monitoring equipment are also connected to the DAQ device.

### 2.2.2 Software

National Instruments Labview software was the major package used for calculation of test parameters. Previous researchers working with this engine devised a well laid out and user friendly set of sub VI's for use in collecting and presenting raw engine parameters, pressure trace data, and emissions equipment responses [52]. These sub VI's were taken and significantly modified for this study to provide real time data. Sub VI's were collected and integrated as one program with multiple functions, tabbed for ease of accessibility and screen manipulation. Specific air density, exhaust composition, and expected particulate matter and oil consumption results sub VI's were created to provide real time data analysis. In addition an extensive set of calculation and correction VI's and equations were integrated to provide proper conditioning of Sulfur Dioxide meter signals and real time oil consumption results as discussed in later sections. The VI's together provide the potential to evolve into an even greater tool for the tracking of mass flow throughout the engine by integration of more specific PM and lube oil consumption modeling algorithms.

An additional simulator report writing and reading function was integrated into the Main VI for use in recalculating raw data results and presenting examples for experimental, educational, and presentation purposes. The figure below shows front panel screenshots taken during a simulated run using a file obtained during an actual test at the B75 condition. Fuel consumption information is assumed and entered on the right center portion of the front "Engine" tab. The HC and CO/CO<sub>2</sub> analyzers were not operating and assumed values are selected using the switch on the lower left corner of the detector's output panel on the "Emissions" tab. Time scales on analyzer charts are in units of seconds and are relative to when

the chart was cleared. All plots depict the same interval in time. Larger screenshot views are included in Appendix B.

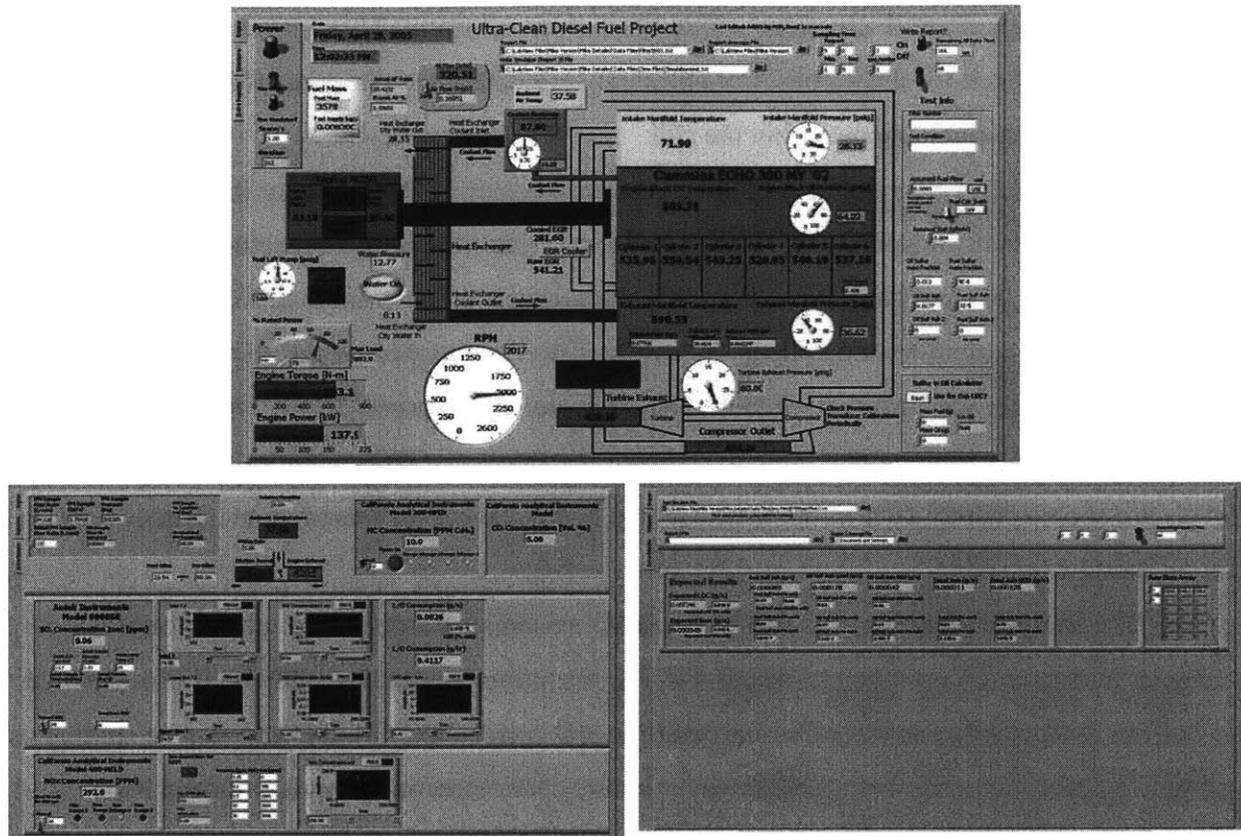


Figure 6 Data acquisition front panel views.

## 2.3 Emissions Analysis Equipment

### 2.3.1 NO/ NO<sub>x</sub> analyzer

Nitrous oxides, as stated previously, are a key pollutant studied on diesel engines. While EGR and other strategies have done much to reduce NO<sub>x</sub> levels they are still emitted at a significant rate. A California Instruments model 400 HCLD was used to measure the NO and NO<sub>x</sub> emissions.

The sampling system consists of a ¼” OD Teflon coated heated sampling line taking suction using an internal sampling pump. The sampling location is located approximately 10 straight pipe diameters downstream of the engine exhaust outlet.

The output from the analyzer was very resistant to temperature and analyzer drift effects. Electrical noise between the analyzer and DAQ system over the range studied was virtually

nonexistent, with sampling normally conducted at one sample per second. In most cases the analyzer maintained  $\pm .5$  ppm<sub>v</sub> NO as checked by span gases throughout an entire day's testing given normal temperature fluctuations within the test environment. This analyzer was also placed outside of the test cell for the purposes of eliminating potential temperature affects from significant ambient fluctuations within the cell.

The analyzer works on the chemiluminescence principle. An ozonator inside the meter converts O<sub>2</sub> supplied from compressed gas bottles to O<sub>3</sub> for the chemical reaction required. Two operation modes, NO and NO<sub>x</sub>, provide the measure of just NO or combined NO and NO<sub>2</sub> respectively. For normal test operations the analyzer was maintained on the NO setting to provide interference gas information to the SO<sub>2</sub> analyzer as discussed below. NO<sub>x</sub> measurements were taken once per running condition to estimate the amount of NO<sub>2</sub> in the exhaust gas. NO<sub>2</sub> levels are approximately 10% of the total NO<sub>x</sub>, so NO is the primary component. This is typical for all diesel engines[8].

The analyzer response was sent to the DAQ system and used for calculation of SO<sub>2</sub> analyzer interference correction as discussed. The chemiluminescence technique is not sensitive to SO<sub>2</sub>, so this provided an ideal tool for real time NO corrections[68]. NO can also be studied using UV absorption characteristics, however in that case corrections would not have been possible given the dual interference.

### 2.3.2 HC Analyzer and CO<sub>2</sub> Analyzer

A California Instruments model 300 HFID HC analyzer was installed on the test engine however malfunctions during most of the testing made it unavailable. Generally speaking the measure of hydrocarbons found during early testing by past researchers was found to be typical for the size and model test engine used. The sampling point for the hydrocarbon analyzer in past studies was the same as that used for the NO<sub>x</sub> analyzer and hence unburned hydrocarbon data from these tests will not accurately detail the presence of hydrocarbon contribution to particulate matter emissions due to tailpipe effects[69]. While hydrocarbons have been found to affect SO<sub>2</sub> detector readings the presence of two furnaces and excess O<sub>2</sub> in the SO<sub>2</sub> analyzer used should combust most unburned hydrocarbons present as discussed in the next section.

A California Instruments model 602P CO/CO<sub>2</sub>/ O<sub>2</sub> analyzer was installed on the system by a fellow researcher for the purpose of monitoring dilution ratios in the exhaust tunnel. While

not used for normal operations in this study the analyzer was useful in confirming the proper operation of the intake air flow meter and determining the exact concentration of O<sub>2</sub> supplied to the SO<sub>2</sub> analyzer.

### 2.3.3 SO<sub>2</sub> Analyzer

#### 2.3.3.1 UV Fluorescence Theory

UV fluorescence is a proven method for measuring trace Sulfur in exhaust to determine oil consumption and has been employed extensively by research labs at auto companies and academia for real time oil studies[21]. Detection of Sulfur using UV fluorescence utilizes the fluorescence characteristics of Sulfur Dioxide. UV light is widely used for pollutant observation due to the lack of absorption of UV light by the major components of air, N<sub>2</sub> and O<sub>2</sub>, and minor constituents including H<sub>2</sub>O and CO<sub>2</sub> at ambient conditions [70]. It is particularly well suited for exhaust analysis and has even been adapted for in cylinder measurement. In cylinder applications require additional corrections to spectral data due to the differences in characteristics of gas absorption at high temperatures[71]. Raman spectroscopy and Fourier Infrared spectroscopy (FTIR) have also been employed in the study of gaseous emissions, with Raman being particularly resilient to atmospheric and exhaust interferences. The figure below depicts the entire electromagnetic spectrum. Absorption spectra for Sulfur Dioxide in the UV range is shown in following figures.

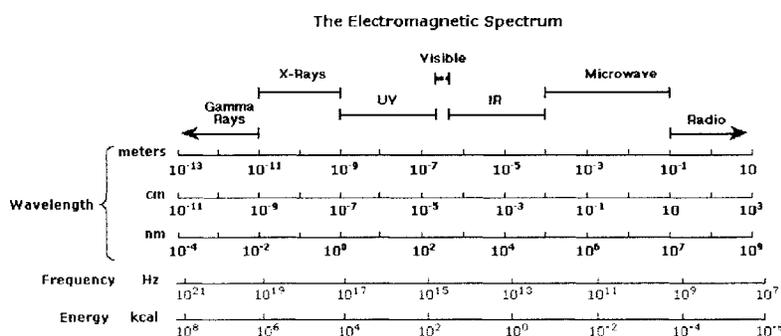
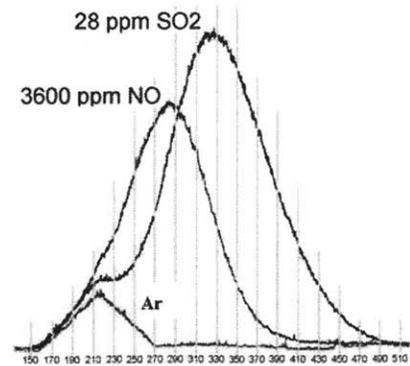


Figure 7 Electromagnetic Spectrum[72]

In this method UV light is used to excite zinc, creating a 214nm source which is passed into the sample gas. The emitted light is passed through an optical filter of 310-380 nm and captured by a photomultiplier tube for creation of a data acquisition signal. The intensity of the emitted and received light is used to determine the amount of Sulfur Dioxide based on the theory described in this chapter. The response spectra for the analyzer based on tests by Antek Industries is indicated in the figure here. Three gases were used, 3600 ppm, NO, 28 ppm, SO<sub>2</sub>, and Ar. The aperture was held open wider than usual providing a non-descript peak at 214nm, which should normally show up as a single line[73].



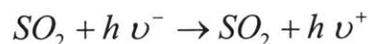
When light is absorbed by a substance it's energy must increase in accordance with the first law of thermodynamics. That energy similarly must be released to return the substance to its original state. Photoluminescence is the term given to describe light emission as a result of light absorption. Bohr's theory dictates that energy increases or decreases in the system in known definite energy levels, unless of course in the case of ionization or dissociation in which enough energy is added to completely separate one part of the system from another[74]. Past research has revealed these levels for most simple atomic and diatomic substances, with many more complicated systems also documented. According to Bohr's theory the transition between two energy levels N, equilibrium, and F, excited, is given by[74]:

$$\nu_{FN} = \frac{1}{h} * (E_F - E_N)$$

$$h = \text{Plank's Constant} \quad E_x = \text{Photon Energy at "x"} \quad \nu_{FN} = \text{Freq of radiation absorbed}$$

The value,  $h \nu_{FN}$ , gives the change in photon energy. For simplicity frequency is often expressed in other terms including wavelength and wave number. The wavenumber is inverse of the wavelength. The frequency is related to the wavelength by  $\nu = \frac{c}{\lambda}$ .

The ideal increase in energy based on absorbance is generally shown in chemical equations for Sulfur Dioxide fluorescence as:



The degree to which light is absorbed is determined by the Beer-Lambert Law, which can be applied to calculate the intensity absorbed or emitted during an absorption and emission process[70].

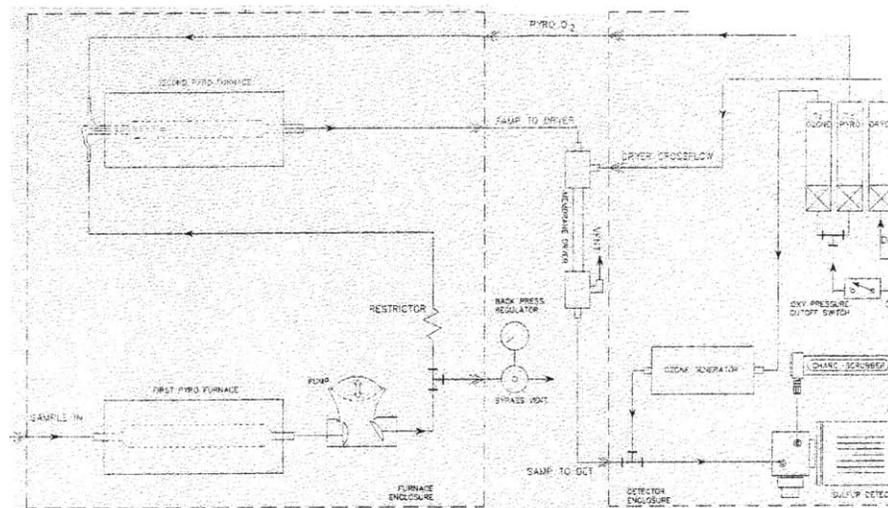
Energy is released from the atom or molecule to return to the ground state through emission or scattering. During emission excitation occurs through an external excitation mechanism, with fluorescence being the special case in which that mechanism is radiative. During fluorescence light is emitted at a state higher than the ground state, and thereby in accordance with Stokes law at a frequency smaller, or wavelength longer, than the original excitation frequency. A special case of fluorescence is phosphorescence, the primary difference between the two being the duration of the process, with the latter lasting longer due to passage through a metastable level[74]. Light emission at the same frequency as that of absorption for direct return to the ground state is deemed “resonance radiation” [74]or “resonance scattering”[70]. Pringsheim is careful to note the characteristics of emission are based on the same scientific principles of energy transfer irrespective of the name given to the process. In addition systems are not in a state of thermodynamic equilibrium at the molecular level when absorbance and emission or scattering is occurring. The molecules being excited reach a higher temperature than those surrounding them. Therefore the process of quenching by other non excited gases is a possible method of energy loss for return to the ground state. Quenching is discussed later.

#### 2.3.3.2 SO<sub>2</sub> Analyzer Specifics

Sulfur Dioxide exhaust gas analyzers differ from other UV Sulfur Dioxide spectroscopy analyzers in their preparation of the sample. Generally UV spectroscopic methods are capable of measuring Sulfur Dioxide levels below 100 ppb<sub>v</sub>, whereas the model used in this exhaust application, given interference effects and sensitivity limitations, has a lower detection limit of 250 ppb<sub>v</sub>. Analysis methods to measure exhaust Sulfur levels below this range have been presented in recent studies and are generally successful through control of interference effects[24, 29].

A diagram of the Antek 6000SE is included below. The sampling hose is connected to stainless steel tubing outside of the analyzer housing. Any metal can adsorb Sulfur as discussed in the section detailing sample collection, however care of the internal Pyrex tubing and hose

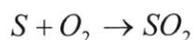
requires proper alignment and pressure regulation prior to entry. A pressure control valve is located on the outside of the instrument to help dampen the affects of engine backpressure changes. This system used a 20 foot sampling line and therefore this affect was not found to be significant, however the pressure control equipment was left as installed for protection of the instrument. The valve was also used in regulating pressures during the changing of standard span gases. The first pyro furnace combusts organic matter and raises the temperature of the sample to 1000°C. A high temperature positive pressure sample pump ensures proper sample volume flow. Maintaining volumetric flow throughout the instrument is crucial given the small sample, measured at .005%-.025% of the exhaust depending on the engine operating condition. In addition the added Oxygen and Ozone flow rates during sample preparation are approximately the same as that of the exhaust sample. To maintain constant volume flow between sampling gases and span gases a manually operated valve is located after the pump to maintain proper backpressure on the downstream restriction.



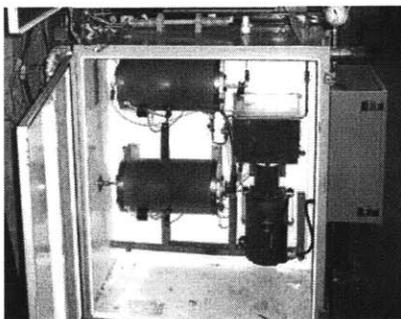
**Figure 8 Antek 6000SE Sulfur Dioxide Analyzer[75]**

Oxygen is supplied to the sample at the inlet to the second furnace. This O<sub>2</sub> serves two purposes. The main purpose is to convert the Sulfur to Sulfur Dioxide[75]. Oxygen quenching is also known to have a greater reduction on fluorescence of nitrous oxides than on Sulfur Dioxides and therefore helps reduce the affects of NO<sub>x</sub> interference as discussed later[76]. The Sulfur to Sulfur Dioxide reaction is most effective at temperatures of 1000°C, the setting of the second furnace. Generally most Sulfur found in diesel exhaust is already in the form of SO<sub>2</sub>, with

smaller percentages present as elemental Sulfur and  $SO_3$ . Reaction of remaining elemental S is based on the following equation:



After the second furnace the sample flows through two nitrogen supplied membrane driers. The first located before the analyzer upper housing and the second located inside this air conditioned upper housing to allow for proper drying after the sample enters the cool atmosphere. The membranes are required to eliminate the absorption affects of water vapor and hence the analyzer response is a dry standard. Water vapor has a greater affect on UV absorption where it is found in excess of ambient conditions and at higher temperatures. In addition it is known to absorb Sulfur Dioxide. The presence of water in the system will lead to spikes and variations in response due to the absorption and release of the  $SO_2$  gas in the sampling system and due to water induced UV variation[68].

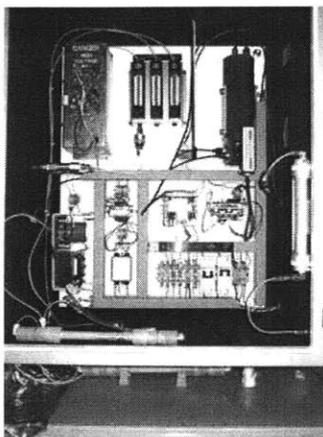


**Figure 9 Sulfur Dioxide analyzer lower box with furnaces and sample pump. The first membrane drier is located on top of the box.**

At this stage Ozone is supplied to the sample from the four cell ozonator located in the upper box. The Ozone is supplied to further reduce the NO present in the exhaust sample prior to entering the fluorescence chamber in accordance with the following equation:



The relationship between  $O_2$ ,  $O_3$ , NO,  $NO_2$ , and  $SO_2$  has a significant effect on correction factors and are described in detail later in this section. After fluorescing the sample is sent through a scrubber to remove Ozone from prior to exhausting to the lab exhaust trench.



**Figure 10 Sulfur Dioxide analyzer upper box. The ozonator is located in the upper left corner, the detector in the upper right.**

#### 2.3.3.3 Error and Interference Control

Quenching effects and interfering gases, discussed below, can alter the readings and must be taken into consideration. To take readings near the 250 ppb<sub>v</sub> lower detection limit on the analyzer considerable care is needed to ensure accurate results. Noise and interference in signal readings are significant.

##### Sampling System Leaks and Drift:

Initial checks of the system were required due to meter idleness over a number of years with several fittings removed. Replacement of the pyrotubes and gas leak checks improved sensitivity considerably. The presence of a gas leak in the system introduces a diluent into the sample stream if the leak occurs prior to the pump. After the pump a leak exhausts a portion of the sample thereby changing the flow rate from which it was calibrated. Leaks manifest themselves primarily by abnormally noisy data due to the fluctuations in leak magnitude imposed by the pump frequency.

General drift of the meter for reasons other than those presented here as interferences was generally minor and below 100ppb<sub>v</sub>. Due to temperature concerns calibration was conducted so frequently that drift was assumed negligible during analysis.

##### Data Acquisition Filtering:

Filtering is required to portray data on the data acquisition system as it appears on the Antek Detector Module. Visual inspection of the detector module indicated that the device outputs approximately three readings per second. This was confirmed by both oscilloscope and

high sampling rate inspection using the data acquisition system. Sampling at rates of 1 Hz indicated significant deviation between module screen outputs and computer DAQ readouts upon initial wiring of the device to the SCXI 1102B module via the TBX 1303 breakout board. Deviations of approximately .2 V were recorded, which in this application are considerable given the ppb accuracy required. Aliasing along with high frequency noise from surrounding lab transformers and power supplies was identified as the cause. Higher level sampling at over 120 Hz confirmed this. To minimize the effect a crude software filter was developed by gathering over 100 samples per second in the data acquisition buffer and averaging them for reading at the VI front panel update rate of one scan per second. The averaging effectively dampened the errors experienced and returned a value which was easily recognized as the average of the 3 samples per second shown on the local detector module. The filter effectively reduces high frequency noise and that generated by the fluctuations output by the module circuitry and that of the analyzer equipment. The filter effectiveness was confirmed by use of a low pass Butterworth filter applied to a waveform generated by the buffered data. The output of the filtered data with frequency cutoffs of less than 20 Hz correlated well to that of the averaging. The effect of low pass filtering by averaging is well documented in mathematical texts and provided for easy application to the data acquisition program[77]. Additional efforts to remove noise included use of shielded cabling on all acquisition wiring and use of common circuits to eliminate fluctuation from ground references. To further smooth the filter for use in real time monitoring and spanning a 10s running average chart was added to the VI. The benefits of more accurate steady state readings outweigh the loss from peak cutoff due to smoothing. Reported values were expressed as the average of steady state readings taken over several minutes. During transient tests the 1s chart will be more useful.

#### Sampling System Materials:

SO<sub>2</sub> detection, as well as Sulfur sampling in particulate matter, is highly sensitive to sampling system composition and temperature. Due to the existing test cell arrangement and the desire to keep the detector in a relatively stable temperature environment a 20 foot sampling hose was required. Sulfur is easily adsorbed by metals, with the most resistive material being stainless steel. Tests by Lizumi and Koyama showed a high adsorption rate of Sulfur Dioxide with a stainless steel furnace material and very little using a quartz furnace. Adsorption increased as a result of increased temperature and concentration [23]. Generally stainless steel's adsorption

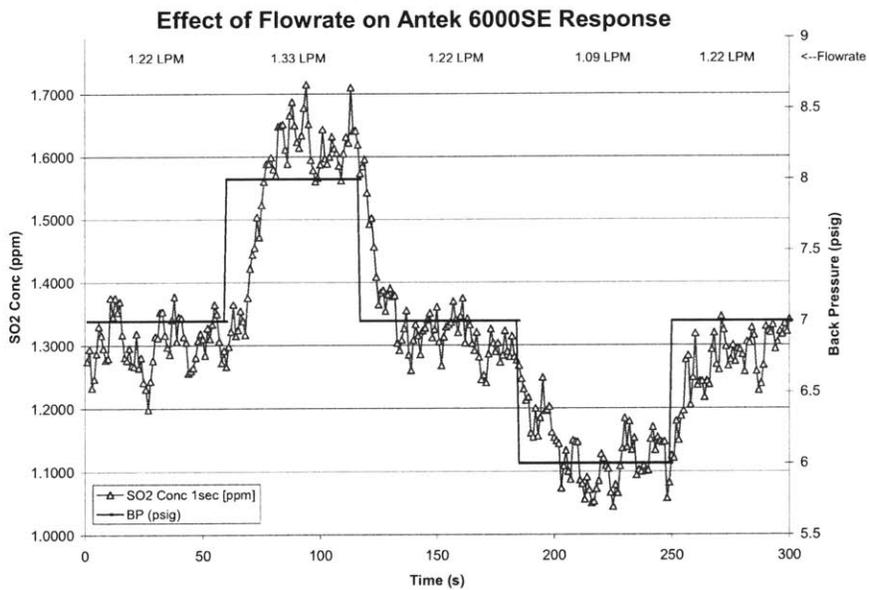
characteristics increase considerably over 150°C[68]. Use of other metals should be avoided altogether. Condensation is also a significant problem in the sampling system due to the tendency for water to absorb Sulfur. Such absorption within the sampling line will result in sharp increases and decreases of output for a given steady state due to the absorption and release of Sulfur over time. Maintaining a sample line temperature over 80°C is required to prevent condensation. To prevent condensation and adsorption error a Teflon coated stainless steel braid heated sampling hose was engineered with the help of and constructed by Technical Heater's Inc to regulate the temperature of the exhaust sample at 150°C. Approximately two feet of stainless steel tubing exists between the sampling hose connection and the furnace inlet to provide for a stainless steel flow control valve and a stable support for the furnace tube. An additional two feet of stainless steel tubing exists between the first furnace and the second furnace, which includes the heated sample pump. Use of stainless steel was required here due to the high temperatures and stability required. The temperatures of the stainless steel tubing directly downstream of the first furnace were measured in excess of 800°C using a thermocouple, leaving this a potential source for adsorption. Even with these efforts initial test results indicated significant adsorption effects as discussed later. For spanning polyethylene tubing and stainless steel fittings were used to prevent adsorption between gas cylinders and the analyzer[78].

#### Flowrate and Pressure:

Studies of UV spectra in the literature indicate calculated spectral responses for flow through gases are consistently lower than those obtained using a stationary gas in a cell[71]. For purposes of an individual analyzer this is unimportant as results are calibrated to the particular relative intensity response of the instrument. Flow rate is still an important parameter for flow through instrument use with changes in flow rate effectively changing ratios of added gases to the sample stream, namely O<sub>2</sub> and O<sub>3</sub>. Lizumi and Koyama showed, and it was confirmed in lab tests here, that the amount of O<sub>2</sub> in the diesel exhaust stream throughout the range of operation allows for a decrease of additional O<sub>2</sub> to the pyro furnace for SO<sub>2</sub> reactions described above. In tests conducted in this study the manufacturer recommended O<sub>2</sub> addition was cut in half to still allow for the benefits of quenching and to increase reaction rates.

Changes in instrument backpressure just after the sample pump can be regulated manually and must be monitored due to drift during experimentation. Even a slight change in backpressure and resulting flow rate can cause significant changes in readings. For the

manufacturer's given parameters the flow rate of the sample is approximately .005%-.025% of the overall exhaust flow, with this accounting for 50% of the overall sample flow given the addition of a comparable volume of O<sub>2</sub>. Adjusting backpressure  $\pm 1$  psig has the effect of altering raw exhaust flow rate to the detector over  $\pm 15\%$ . The following figure shows results of a test of these effects during experiments with sulfated fuel. The backpressure scale is included on the right, with the corresponding overall flowrates (sample plus added constant flow of 90% O<sub>2</sub>) given along the top of the graph.

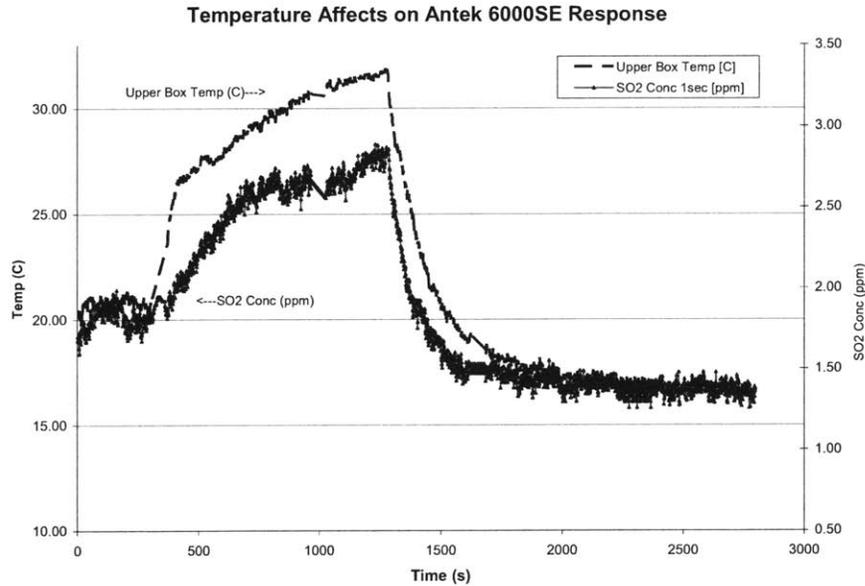


**Figure 11 Effect of Flow rate Changes on Antek 6000SE Response**

Temperature:

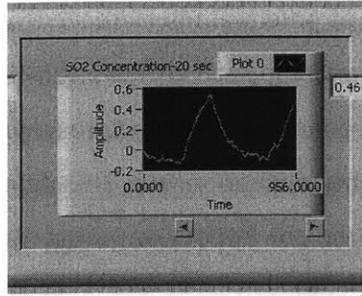
Temperature of the upper box containing the ultraviolet detector has a significant effect on response as well. According to the manufacturer errors of 25% will result from a 15°C temperature change in one day. Tests on the instrument revealed significantly greater errors can occur at low SO<sub>2</sub> concentrations. A thermocouple was placed inside the upper box for constant temperature tracking during testing. The following figure shows the affect of temperature changes instigated by manipulation of the air conditioner and upper box door position during testing with sulfated fuel. Inlet sample temperature and flow rate were held constant during this

test. The upper box temperature scale is indicated on the left, with the SO<sub>2</sub> concentration, already adjusted for NO, indicated on the right.



**Figure 12 Temperature Affects on Antek 6000SE**

Similar errors are apparent with span gas sampling, indicating an approximate change of over 1 volt (1 ppm<sub>v</sub> SO<sub>2</sub>) for each 10°C change. Hence, a 16°C change would indicate a 2 volt change, 20% of the meter's range, which is consistent with the manufacturer reported error. Therefore the error does not appear to be based on a percentage of the given reading but on an absolute change. This was confirmed by an earlier test in which the box door was opened and closed with the meter zeroed. The thermocouple had not been installed at this time, however the screen capture shown in the next figure indicates the response. The temperature change in this test, measured using a standard glass thermometer was approximately 5°C. Therefore, for measurement range below 1 ppm<sub>v</sub> temperature induced error can be extreme.



**Figure 13 Data acquisition screen capture. Temperature influence on detector reponse at zero SO<sub>2</sub> condition.**

To prevent temperature error the meter was placed outside of the engine test cell and the upper box temperature was continuously monitored. Tests were run with the meter running within  $\pm 1^{\circ}\text{C}$  of the spanning condition. This was easily achievable while running the air conditioner constantly and waiting one hour between warm up and experimental runs. A fan was placed forward of the meter to create a light air flow between the upper and lower boxes, this effectively preventing excessive heat transfer between the two boxes which can cause temperature changes over time from warming of the lower wall of the upper box. Temperature inside the upper box using these procedures may still fluctuate of  $\pm 3^{\circ}\text{C}$  between engine operating conditions. Therefore during SO<sub>2</sub> mapping in which operating conditions were changed frequently over the course of a day calibration was repeated at nearly every test condition.

#### Interference Gases:

UV spectroscopy techniques continue to be studied for greater understanding and quantification of the UV absorption and emissions spectra of various gases, particularly those of complicated substances and mixtures. While knowledge of specific spectral response is not required for operation of an SO<sub>2</sub> detector an elementary education in the response of the relevant gases to UV light in this range is helpful in quantifying errors in measurement and fluctuations in sensitivity. Considerable work has been conducted to determine UV absorption spectra for application to atmospheric studies. A great deal of information has been published regarding the relative intensity of responses of gases commonly found using satellites and ground based equipment to determine atmospheric composition for large scale air quality measurement. Application of this data to exhaust components derived from air is therefore possible. In addition considerable references exist regarding the spectral responses of organic compounds providing

valuable information on the effects of potential interference from hydrocarbons. A valuable source of data regarding atmospheric compounds is the High-Resolution Transmission Molecular Absorption Database (HITRAN), a compilation of spectroscopic data used by computer codes to predict responses of known atmospheric components. This data, which is being gathered in an ongoing long term study started by the Air Force Cambridge Research Laboratories (AFCRL) in the 1960's, is available to the public[79].

#### NO, O<sub>3</sub>, O<sub>2</sub>, and NO<sub>2</sub> Effects:

NO is the most significant interferent to the Sulfur fluorescence technique given its similar absorption and fluorescence range to that of SO<sub>2</sub>. The similar absorption responses are clearly visible in the previous figure indicating the detector response to 3600 ppm<sub>v</sub> NO. Similar trends can be seen in general plots showing relative spectral responses of gases in this UV range. NO effects, without the use of the ozonator, were measured using 1000 ppm<sub>v</sub> NO<sub>x</sub> at a reading of 3.33 ppm<sub>v</sub> SO<sub>2</sub>. While considerably less than the 100ppm<sub>v</sub> NO:1 ppm<sub>v</sub> SO<sub>2</sub> ratio expected given the manufacturer supplied information it is still very significant. Corrections for NO<sub>x</sub> interference can, in theory, be obtained by direct subtraction mathematically as supported by the work of Mohn and others[10, 76]. The interaction affects of NO<sub>x</sub> and SO<sub>2</sub> in relation to their fluorescence characteristics are not perfectly understood and use of the ozonator should provide a greater reduction of interference by these gases[68]. It has been suggested that reduction of interference gases to as low as 5% is preferable to get accurate readings due to the changes encountered with luminescent meters over various temperature and concentration ranges[80].

Proper use of the ozonator requires a delicate balancing act given the complicated fluorescence and absorption characteristics of the gases involved. Ozone is created in the ozonator using a spark generated by a pulsating voltage whose duty cycle is controlled by the circuit card. Manipulation of the card governs the amount of Ozone produced, with high duty cycles significantly reducing the card life. With the NO<sub>x</sub> range of the test engine the settings used did not excessively load the circuit card by heating, as determined by measurement of the temperature of the heat sink on the card's single transistor. While Ozone can be produced to fully react with NO across the entire range expected in the exhaust the production of too much Ozone can be detrimental as well. For this reason the initial calibration technique of simply increasing the Ozone until the NO response was eliminated created errors in initial exhaust readings using

low Sulfur fuel and oil during shakedown. Exhaust readings returned a negative response on the order of .5 ppm<sub>v</sub> after zeroing with ambient air then switching to exhaust. After discussions with Antek personnel and further research the cause was believed to be the presence of excess NO<sub>2</sub> after reaction with O<sub>3</sub>. NO<sub>2</sub> does not fluoresce however it was suspected of having a higher absorption rate than the O<sub>3</sub> it replaced. A review of the absorption spectra indicate that in the UV range O<sub>3</sub> absorbs at an order of magnitude greater than NO<sub>2</sub>. Despite this reductions of ozonator output to levels just sufficient to counter expected NO<sub>x</sub> seem to eliminate the phenomenon.

Antek advised against using negative responses for calculations given the fact that the electronics are not designed to measure in this range. A practice of calibrating the Ozonator for given test conditions was incorporated prior to each run. The goal is to provide a response to the expected NO rate which is slightly positive. Using two span gases, one just below the expected amount for the test condition and one greater than the amount, a range of attenuation from the NO response can be measured. The lower span gas is used to return a slightly positive NO response. This ensures that sufficient O<sub>3</sub> is generated to convert NO to NO<sub>2</sub>, while some NO is left to fluoresce and counter any effects of increased absorption of NO<sub>2</sub>. This effectively makes O<sub>3</sub> the limiting reactant and allows for corrections. Calibrations were set such that NO attenuation was on the order of .1-.2 ppm<sub>v</sub> SO<sub>2</sub> for the expected test range. Linear and polynomial curve fits were calculated for the NO response of the span gases and applied in real time using the NO analyzer generated response in Labview. Generally the NO reaction is not linear, hence the use of an NO span gas close to that actually observed is important. Over the majority of conditions tested on this engine the NO response was on the order of 100-300 ppm<sub>v</sub>, a range at which the 6000SE O<sub>3</sub> generator can be set to eliminate NO induced SO<sub>2</sub> in its entirety. Some test conditions, such as low speed high load, did produce NO at a range of 2200 ppm<sub>v</sub>. NO<sub>2</sub> contribution was measured at various test conditions and was found to be on the order of 10% or less of the NO response. The NO response was converted to a dry standard prior to use for correcting SO<sub>2</sub> concentrations.

Oxygen is also known to have an affect on SO<sub>2</sub> response. O<sub>2</sub> is added to the sample gas in the second pyro furnace as a catalyst to the creation of SO<sub>2</sub>. This is particularly important in SI engines utilizing near stoichiometric air fuel ratios. In the diesel application sufficient O<sub>2</sub> is often present in the gas stream to negate the need for addition of O<sub>2</sub>[23]. The test engine exhibits O<sub>2</sub> levels in the exhaust of 11% to 18% over the entire range of speeds and load tested. The

manufacturer recommended settings of an additional .65 LPM of 90% O<sub>2</sub> constitute an increase to 66%-70% of the sample flow consisting of O<sub>2</sub> leaving the second furnace. Additional oxygen is added when the O<sub>3</sub> gas stream, which is created from a .25 LPM flow of O<sub>2</sub> across the ozonator, is added. While much of the O<sub>2</sub> is converted to O<sub>3</sub> in the ozonator the conversion is not complete. In addition some O<sub>3</sub> is converted back to O<sub>2</sub> after leaving the ozonator. It was found that reducing the O<sub>2</sub> concentration by half, effectively reducing the combined sample/O<sub>2</sub> concentration to 47%-51%, did not change the SO<sub>2</sub> concentration readings at similar engine conditions. It did allow a reduction in the span dial setting, an effective increase in overall sensitivity by 20%. While in theory enough O<sub>2</sub> may exist in the exhaust sample to produce SO<sub>2</sub>, residence time and quenching effects also play a role by addition of O<sub>2</sub>. Increasing O<sub>2</sub> should maximize SO<sub>2</sub> formation by shifting the equilibrium equation to the production of SO<sub>2</sub>. O<sub>2</sub> has also been found to have a greater quenching effect on NO than on SO<sub>2</sub>, hence providing additional decreases in NO interference[76]. In a study by Mohn et al O<sub>2</sub> was added to increase total sample percentage to approximately 20%, with increases in fluorescence intensity observed with decreases in O<sub>2</sub> added. This is consistent with the reduced span dial gain requirement observed and discussed earlier.

#### Formaldehyde and Hydrocarbons:

Additional gases are known to affect UV readings. Organic hydrocarbons are frequently studied using UV absorption as indicated by the large amount of data published on their spectral characteristics. Formaldehyde in particular has been found to affect fluorescence measurements of SO<sub>2</sub>[76]. In studies identifying formaldehyde errors lower detection levels were frequently below the 100ppb<sub>v</sub> range and oxidation and drying of the sample had not been conducted to remove volatiles. While diesel is known to be a greater producer of formaldehyde in gas form as compared to gasoline FT fuel has been shown to have significantly reduced levels[81, 82]. This combined with the oxidation of the first and second furnaces should reduce this interference to well below detectable levels. Initial tests indicated exhaust responses using low Sulfur fuel and oil were on the order of negative .5 ppm<sub>v</sub> as explained earlier. Reduction of ozonator output removed this negative response, indicating O<sub>3</sub> concentrations or potential relative flowrate differences were the cause of the deviation. This does not rule out a reaction due to hydrocarbons and O<sub>3</sub> which warrants further study.

### 2.3.3.4 Calculating Lube Oil Consumption

To calculate the lube oil consumption the SO<sub>2</sub> concentration in the exhaust was used to estimate the amount of oil combusted or otherwise released into the exhaust stream. While EGR was not varied for this test a significant change should not occur based on a simple mass balance. The only exception to this would be in the event of Sulfur adsorption in the EGR and turbocharger equipment. EGR's reduction of NO emissions in particular should make it an asset to the Sulfur Dioxide tracer process.

The following derivation is included to demonstrate the application of the mass balance equation and NO correction coefficient to the calculation of the oil consumption rate. Symbols and format closely follow that detailed by Yilmaz for simplicity[12] and resemble in solution those of several other works including Schofield[20]. Defining the entire engine as our system with a control volume encompassing the prime mover on the downstream flow side of the fuel and air intakes to the exhaust tailpipe after the turbocharger and EGR, we can apply the conservation of mass to characterize the system as follows:

$$\dot{m}_f + \dot{m}_a + \dot{m}_o + \dot{m}_w = \dot{m}_{w,e}$$

$\dot{m}_f$  = mass flow fuel

$\dot{m}_a$  = mass flow air

$\dot{m}_o$  = mass flow oil  
consumed

$\dot{m}_w$  = mass flow engine wear particles

$\dot{m}_{w,e}$  = mass flow wet exhaust

Applying the proper mass fractions of Sulfur composition to these components and assuming the effects of absorption by water and metallic components are zero we can determine the mass of Sulfur generated by each mass flow constituent and hence the total Sulfur in the wet exhaust. Since air drawn from the test cell is used as a zero sampling gas the Sulfur content of air can be assumed to be zero. The use of test cell air is preferred to prevent errors caused by vaporization of Sulfur from small fuel or oil leaks as well as the presence of Sulfur or NO from the presence of minor exhaust leaks which may exist and become entrained in the air intake which is within the test cell.

It is assumed that the presence of Sulfur in any hard metal wear particles drawn into the exhaust stream is also zero. In actuality the adsorption and release of Sulfur from these particles, engine components, and any water entrained in the exhaust sample would cause variations in measured content for any given time.

The simplified mass balance of Sulfur is therefore:

$$\xi_{s,f} \cdot \dot{m}_f + \xi_{s,o} \cdot \dot{m}_o = \xi_{s,we} \cdot \dot{m}_{w,e}$$

$\xi_{s,f}$  = mass fraction Sulfur in fuel

$\xi_{s,o}$  = mass fraction Sulfur in oil  
consumed

$\xi_{s,we}$  = mass fraction Sulfur in wet  
exhaust

The mass of oil consumed is given by:

$$\dot{m}_o = \frac{\left[ \xi_{s,we} \cdot \dot{m}_{w,e} \right] - \left[ \xi_{s,f} \cdot \dot{m}_f \right]}{\xi_{s,o}}$$

In this equation the mass fraction of Sulfur in the oil is assumed to be known. This is most commonly accomplished by using the fraction as calculated by ASTM D4294. To ensure Sulfur is released equally from light and heavy oil species over the entire range of distillation the oil can be subjected to stepwise distillation in accordance with ASTM D5236 and its Sulfur content measured at different volume distillation percentages. Using this value estimates of final lubricant consumption may be lower than expected due to adsorption losses of Sulfur due to different sampling system effects as discussed earlier. For this reason a modified Sulfur fraction was used for increased accuracy in this study as described in Chapter Four. The remainder of the terms in the above equation are derived from experimental results as follows:

The mass flows of fuel and air are calculated directly as discussed in other sections. For the purposes of the mass calculation of wet exhaust the mass of oil consumed is assumed to be a negligible fraction and therefore zero. This assumption is supported by the typical oil consumption ratios for diesel engines which range from 1-30 g/hr. At this rate the oil consumed accounts for a maximum .004% exhaust over the range of test conditions. Similarly the mass of engine wear debris is assumed to be zero.

In the absence of a fuel flow meter or gravimetric measurement as used in this study a similar equation for wet exhaust mass flow can also be estimated using the stoichiometric ratio of the fuel used, identified here as  $L_{st}$ , and the relative air fuel ratio,  $\lambda$ , (as defined in Heywood and other texts):

$$\dot{m}_{w,e} = \dot{m}_f + \dot{m}_a = \dot{m}_a \cdot \left[ 1 + \frac{1}{L_{st} \cdot \lambda} \right]$$

The Sulfur Dioxide reported by the meter is on a dry basis in parts per million by volume which can be assumed to be the volumetric fraction of dry exhaust. The molar fraction of Sulfur Dioxide, taken from the meter and given by  $\psi_{d,uncorr,SO_2}$ , must be corrected for the SO<sub>2</sub> response contributed by the NO in the exhaust. The NO meter reads NO on a wet exhaust basis in parts per million,  $\psi_{w,NO}$ , and therefore a correction must be applied to this reading to convert to NO on a dry basis,  $\psi_{d,NO}$ . For this test engine the exhaust water molar fraction,  $\psi_{H_2O}$ , was calculated at 2 to 7% over the full range of operating conditions. This correction could also be applied after the Sulfur response is converted to a wet basis, however for programming simplicity this method was used to allow for a reading of the actual (wet) ppm<sub>v</sub> SO<sub>2</sub> prior to lube oil consumption calculations. To determine the total water content in the exhaust the simple combustion equation molar fraction calculation was modified to account for the slight differences in ambient air humidity. Given the large quantity of air present in lean diesel mixtures this can play a greater roll in exhaust water content over SI engines. The value for  $\lambda$  is derived from an air fuel ratio based on a calculation of air mass flow using the wet component of air flow. The molar fraction of water is also calculated based on the wet and dry basis densities and used to add the moles of water present in the air to both sides of the combustion equation. For calculation of molecular weight, mass flow, and density a wet basis air mass flow is used. The total water content of the exhaust is therefore given by:

$$\psi_{H_2O} = \frac{n_{air\ water} + n_{combustion\ water}}{n_{exhaust}}$$

$$n_{air\ water} = \text{moles water from air} \quad n_{combustion\ water} = \text{moles water from combustion} \quad n_{exhaust} = \text{total moles exhaust}$$

The corrected SO<sub>2</sub> concentration based on NO is therefore:

$$\psi_{d,corr,SO_2} = \psi_{d,uncorr,SO_2} - [\psi_{w,NO} * (1 + \psi_{H_2O})]$$

To calculate the molar fraction of Sulfur Dioxide in the wet exhaust the molar fraction of water is again used from exhaust calculations.

$$\psi_{w,SO_2} = \psi_{d,corr,SO_2} * [1 - \psi_{H_2O}]$$

The Sulfur fraction in the wet exhaust can now be determined based on the molecular weights of the wet exhaust, SO<sub>2</sub>, and elemental Sulfur given as  $M_{w,e}$ ,  $M_{SO_2}$ , and  $M_S$  respectively.

$$\xi_{s,we} = \psi_{w,SO_2} * \frac{M_{SO_2}}{M_{w,e}} * \frac{M_S}{M_{SO_2}}$$

Substituting the equations above into the first we can derive an equation for the lubricant oil consumption. This equation was coded into Labview for use in the continuous data acquisition software.

## 2.4 Ambient Air Measurement and Flow Calculations

### 2.4.1 Air Flow

Intake air is drawn from inside the test cell and flow is measured using an Eldridge products series 8732 thermal mass flow meter installed in well developed flow upstream of the turbocharger. Volumetric flow rates are converted to mass flow in real time as described in the following sections. Since air flow is constantly measured and steady state conditions are run the uncertainty of the air flow meter is assumed to average out over time. This uncertainty based on variability of the air flow is accounted for in the calculated PM uncertainty by calculation of the standard deviation of the percent of exhaust sampled. The total exhaust is calculated by summing the air and fuel masses, therefore the air flow measurement is a significant parameter.

### 2.4.2 Air Temperature and Humidity

Air temperature and relative humidity were measured constantly with an Omega digital thermo-hygrometer at a sampling point approximately one foot from the intake air filter. These values were used in the calculation of air and exhaust densities. Similar to the discussion above on air flow uncertainty these values affected the measurement of the percentage of exhaust flow sampled.

### 2.4.3 Calculation of Air Density

The calculation of air density can be a factor over the range of ambient temperatures experienced in the test cell, changing as much as 5% in the course of a day's testing. Volumetric air flow was converted to mass flow in Labview using an algorithm for conversion dependent on pressure, temperature, and relative humidity. The algorithm was derived using the equation for air density presented in a National Institute of Standards report [83]. The first term can be used independently to determine the dry air density if desired. The general equation is given by:

$$\rho_{air} = \left( \frac{P_{air} * M_{air}}{R_{air} * T_{air} * Z_{air}} \right) * \left[ 1 + (\epsilon - 1) * \frac{e'}{P_{air}} \right]$$

$P_{air}$  = Absolute pressure of air (Pa)       $T_{air}$  = Temperature of air (K)       $M_{air}$  = Molecular Weight Dry Air  
 $R_{air}$  = Universal Gas Constant Air       $Z_{air}$  = Air compressibility factor       $e'$  = Effective vapor pressure water

### 2.4.4 Calculation of Exhaust Density

A similar equation was used for the calculation of exhaust density. The second term in the above equation was eliminated due to the saturation of exhaust with water as indicated by the balancing of the combustion equation. Water content is accounted for in the calculation of molecular weight of the constituents based on the equation. These consist of ambient water and combustion derived water as described in the previous sections. Trace constituents such as NO<sub>x</sub>, NO<sub>2</sub>, CO, Particulate Matter (PM), unburned hydrocarbons (UHC), and SO<sub>2</sub> are considered negligible for the ultimate calculation of exhaust density. These compounds and combustion products, while significant from an environmental and health standpoint, are not significant in the calculation of exhaust properties. As a result of the exclusion the molecular weight for 'atmospheric Nitrogen', 28.16, was used as opposed to the pure diatomic molecular weight of 28.01 for N<sub>2</sub>. EGR fraction is likewise not expected to have a significant effect since the ideal mass balance ultimately encloses the entire engine in the control volume chosen. EGR is responsible for reductions in NO<sub>x</sub> and other compound formations however the exclusion of these compounds negates this effect in calculation of molecular weight and density. In addition the possibility of loss of some of the exhaust due to condensation on fittings throughout the system is assumed to be negligible and was kept to a minimum through use of heated hoses with inert linings as discussed in other sections of this report.

## 2.5 Fuel and Lubricant Properties and Flow Measurement

### 2.5.1 Fuel

A single fuel was chosen for the primary test matrix. A Fischer Tropsch (FT) diesel fuel supplied by Syntroleum was used for its extremely low Sulfur and ash content. This simplified troubleshooting and analysis by reducing the effect of a fuel correction to the mass balance equation when tracing the Sulfur content in the exhaust. FT fuel contains <.001%<sub>wt</sub> ash, making it a good candidate for tests of oil derived ash since most of the contribution will be from the lubricant. The fuel was treated with an additive package consisting of a proprietary formula from Lubrizol Inc at 300 ppm<sub>w</sub>. Information was made available by Syntroleum to determine the Sulfur and additive affects on the parameters of interest in this study[84]. Fuel Sulfur levels were measured by Syntroleum at less than 100ppb<sub>w</sub>, with a theoretical value of less than 50ppb<sub>w</sub>. The extra Sulfur calculated was attributed by Syntroleum to container contamination. At these levels the contribution of fuel to the exhaust stream at its highest is on the order of 4 ppb<sub>w</sub>, a small fraction of the 250 ppb<sub>v</sub> lower detection limit of the Antek 6000SE.

FT fuel is composed of 15.1% Hydrogen and 84.9% Carbon by mass with no Oxygen, Nitrogen, or other impurities[30]. The reduced chemical equation for the fuel therefore becomes CH<sub>2.12</sub> leading to the combustion formula of:

$$\begin{aligned}
 14.49 \text{ CH}_{2.12} + 22.17 \lambda_{wet} \left(1 - \psi_{\text{air}}^{\text{H}_2\text{O}}\right) (O_2 + 3.773 \text{ N}_2) + \left[22.17 \lambda_{wet} \psi_{\text{air}}^{\text{H}_2\text{O}} (4.773 \text{ H}_2\text{O})\right] \rightarrow \\
 14.49 \text{ CO}_2 + 15.36 \text{ H}_2\text{O} + 22.17 \lambda_{wet} \left(1 - \psi_{\text{air}}^{\text{H}_2\text{O}}\right) \left[\left(1 - \left(\lambda_{wet} - \lambda_{wet} \psi_{\text{air}}^{\text{H}_2\text{O}}\right)^{-1}\right) O_2 + 3.773 \text{ N}_2\right] \\
 + \psi_{\text{air}}^{\text{H}_2\text{O}} * \left[22.17 \lambda_{wet} (4.773 \text{ H}_2\text{O})\right]
 \end{aligned}$$

Additional properties include a lower heating value of 43.7 MJ/kg, specific gravity of 775 kg/m<sup>3</sup>, flash point of 61°C, and Cetane index of 74.4. There was no detectable aromatic or olefin content. In separate studies FT fuel was shown to reduce particulate matter by over 50% as compared to low Sulfur fuel (400 ppm<sub>w</sub>)[52]. A significant portion of the particulate matter reduction in this study was attributed to reduced Sulfur content, however Llaniguez also demonstrated through pressure trace analysis a faster burn rate for FT in the latter part of the combustion cycle which would also account for PM reduction. A sample of raw PM taken during

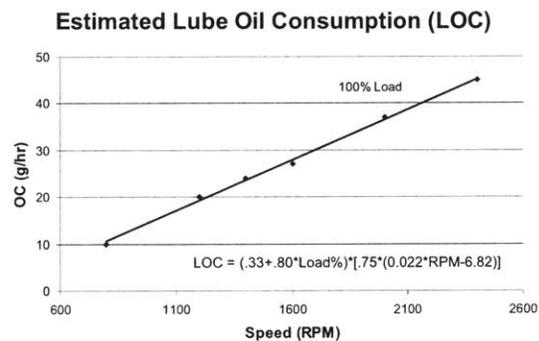
higher Sulfur fuel testing was used during ash calculations later in this study to estimate fuel effects.

Fuel consumption is measured using an Ohaus Scout Pro 6000g scale and a Pyrex beaker. This method allows flexibility in testing by allowing researchers to produce specific mixtures of fuels and lubricants when desired. Several supply and exhaust fans in the test cell ensure proper ventilation for the safety of researchers and to prevent contamination of intake air by any evaporating product from this method. Two separate fuel tanks located just aft of the engine provide supply for normal operation. They separate FT from Sulfur containing fuels and contaminated return fuels. Different fuel filters are used for studies involving Sulfur fuels and straight FT fuel. The SO<sub>2</sub> concentration in the exhaust stream fell below the lower detection limit of the analyzer in under five minutes when switching from Sulfur to FT fuel. To ensure proper flushing FT fuel was run through the engine and all supply and return lines for several minutes prior to changing blends or fuel types. During flushing all return fuel was returned to the sulfated fuel tank to ensure FT fuel was not contaminated. In addition during blending tests fuel was returned to this tank for several minutes prior to placing the return line in the beaker to prevent dilution from fuel already existing in the system prior to the fuel type switch.

### 2.5.2 Determining Required Oil

To obtain an oil suitable for Sulfur Dioxide tracing using the available equipment a high Sulfur content is required. To determine a suitable Sulfur content for testing Cummins provided baseline data for the engine was used along with estimates of oil consumption based on studies in literature. Diesel engines of the size studied typically consume 1-50 grams of oil per hour depending on test and engine conditions [16, 21-23, 35]. A study in literature of a Navistar 7.6 L diesel producing 10-45 g/hr was used as a basis for a rough model of expected lubricant consumption [22]. Scaling these

values based on the displacement of our test engine we expect an oil consumption rate of



**Figure 14 Estimated oil consumption model based on literature results. (Included in Appendix C)**

roughly 75% of this reported value. Taking this information and combining it with oil consumption data gathered on a smaller spark ignition engine at MIT it was assumed that at a constant load oil consumption varied linearly with given speed. Likewise at a constant speed a linear three fold increase in oil consumption can be expected from 25% to 100% of load[12]. Using these parameters a crude estimation of oil consumption was calculated based on engine speed and load conditions. A plot of the expected oil consumption is shown above. Despite the linear trends demonstrated on these engines, many studies have shown that some engines have higher lube oil consumption at certain engine operating conditions not necessarily consistent with increasing speed and load[21].

The model was entered into the following equation which is based on that derived for lube oil consumption in the preceding section. The estimated fraction of Sulfur in wet exhaust was assumed to be the lower detection limit of the analyzer, 250ppb<sub>v</sub>. The fuel Sulfur fraction was assumed to be zero.

$$\xi_{s,o} = \frac{\left[ \xi_{s,we} * \dot{m}_{w,e} \right] - \xi_{s,f} * \dot{m}_f}{\dot{m}_o}$$

Across the entire range of test engine operation it was determined that a minimum content of 1%<sub>wt</sub> Sulfur was required to generate a 250 ppb<sub>v</sub> SO<sub>2</sub> concentration in the exhaust stream. Increased air and fuel requirements for greater speeds and loads offset the anticipated oil consumption increase resulting in a relatively constant Sulfur concentration requirement. As a result a 2%<sub>wt</sub> Sulfur oil was sought to provide for increased response and offset errors from Sulfur adsorption. The understandably proprietary nature of oil composition makes the determination of Sulfur content using published specification sheets difficult. Typically sulfated ash and viscosity data are reported with specific elemental composition excluded. In a review of literature of over 50 commercial oils only 2 reported the Sulfur content. In each case the content was below .5%<sub>wt</sub> (5000 ppm<sub>w</sub>) as expected.

### 2.5.3 Oils Chosen

Two oils were used for testing. The first was a 15W40 commercial lubricant with a 1.00% sulfated ash level. This lubricant had already been used in previous studies conducted on this equipment so it provided a good baseline oil to begin with. The relatively low sulfated ash content provided a good comparison to the sulfated ash level in the other experimental oil as well. Since this oil was not doped with Sulfur the levels of Sulfur in the blend were expected to be too low to be measured by our analysis equipment. The use of an immeasurable oil for consumption measurements was intended to allow for the comparison of the higher Sulfur oil with a commercial oil control. An estimate of the amount of Sulfur in the oil was made by doping the test fuel with a small portion of lubricant, sufficient enough to create a measurable response.

The second oil used was a high Sulfur commercial oil of the same commercial grade. This oil contained over 2% Sulfur by weight, making it an ideal candidate based on our tracing requirements. A 1.77% sulfated ash level also gave this oil high expected ash emission allowing for comparison to the previous oil. Since the two oils are not identical in regards to properties other than sulfated ash a direct comparison cannot be made. The high Sulfur oil manufacturer claims high film thickness of the oil provides for decreased oil consumption and increased power output. For this reason oil consumption values for this oil as calculated are potentially lower than those of the control oil which has a decreased film thickness. A determination of volatile organic fraction in raw PM emissions later determined a similar oil consumption rate is likely for the two oils at mid and high speed and load test conditions.

The following table shows the properties of the fuel and oil used. Additional information was available and is excluded for proprietary reasons.

**Table 6 Test fuel and oil properties.**

	Method	FT Fuel <sup>2</sup>	Low Sulfur Oil	High Sulfur Oil
Specific Gravity, 15°C	ASTM D 4052	.771	.880	.884
API	ASTM D 4052	52	28.2	28.6
Flash Point ( °C)	ASTM D 93	64	228	224
Viscosity cSt@40°C	ASTM D 445	2.1		115
cSt@100°C	ASTM D 445	1.0		15
Cetane Index	ASTM D 976	>74		
Distillation,IBP,10% <sub>v</sub>	ASTM D 86	160°C	-	-
90% <sub>v</sub>	ASTM D 86	601°C	-	-
Ash ( % <sub>w</sub> )	ASTM E 1131 ASTM D 482	<.001	<1.10>	<1.65>
Sulfated Ash ( % <sub>w</sub> )	ASTM D 874	-	1.00	1.80
Aromatics, Olefins, Saturates (% <sub>v</sub> )	ASTM D 1319	nd	-	-
Sulfur ( ppm <sub>w</sub> ) <sup>3</sup>		.09 [84]	<4200>	20300
Viscosity Index			140	142
TBN mg <sub>KOH</sub> /g	ASTM D 2896		10	10.8

## 2.6 Particulate Matter Measurement

### 2.6.1 Dilution Tunnel and Filter Holder

The particulate matter collection system on the engine test bed was designed to carry out tests in accordance with 40CFR86 [85]. The system consists of a mini dilution tunnel consisting of 3” OD SSL 304 tubing, with exhaust gases sampled from the main exhaust pipe through a ¾” OD SSL tube and valve. The purpose of the dilution tunnel is to simulate ambient conditions for emissions measurement and provide time for agglomeration, adsorption, and nucleation of particulate. This dilution tunnel was used in several previous studies to estimate particulate matter as defined by EPA standards.

During this study a separate sampling line was used to draw raw exhaust through the filter holder. This more closely simulates tail pipe conditions which present in a DPF and

<sup>2</sup> These are ‘typical values’ as reported by Syntroleum data sheet.

<sup>3</sup> Estimates in brackets <> represent values measured as part of this study.

increases sampling times. Raw sampling presents particular challenges and degrees of error on account of several factors. Particulate sampling of raw exhaust tends to give lower estimations of PM emission than use of diluted exhaust. Comparisons to previous tests were made for estimation purposes. Higher temperatures in exhaust sampling systems are known to affect particulate agglomeration and the adsorption of sulfates and hydrocarbons on PM particles. In addition higher exhaust tailpipe temperatures reduce PAH and UHC levels due to longer residence times in the high temperatures. At 180°C UHC was found to decrease at a rate of 10-25% over a distance of 30m of tailpipe, then reach a steady state for greater lengths. The affect is greater at increased speeds and loads. Similar effects were noted on particulate matter, SOF, and Carbon concentrations [69]. On the test engine studied exhaust temperatures were monitored at the end of the 3m tailpipe and ranged from 150°C to 400°C prior to drawing into either raw or dilution sampling ports. An additional 3m of raw sampling pipe or dilution tunnel led to the filter holder. For this reason UHC and PAH levels will be lower than actual engine out values using either method. Abbas et al also showed a relative concentration increase of SOF at distances exceeding 7m, and increases in relative concentrations of particulate and SOF in a dilution tunnel. For this reason particulate matter and SOF derived species will likely be higher if collected via dilution tunnel rather than raw exhaust line.

Particulate matter was drawn through the sampling system using a vacuum pump capable of reaching initial flow rates over 200 LPM. A 47mm stainless steel filter holder with Teflon O-rings was used. The holder effective filtration area is 9.6 cm<sup>2</sup>, however qualitative observation of some of the samples in which metallic gasket pieces were found indicated that heavier metallic species might be more likely to be captured in the center of the filter vice points at a greater radius. Flow rates were measured with an Omega FVL-1611 flow meter installed downstream of the filter. Flow rate data was sent to the data acquisition system for real time calculation of the percentage of

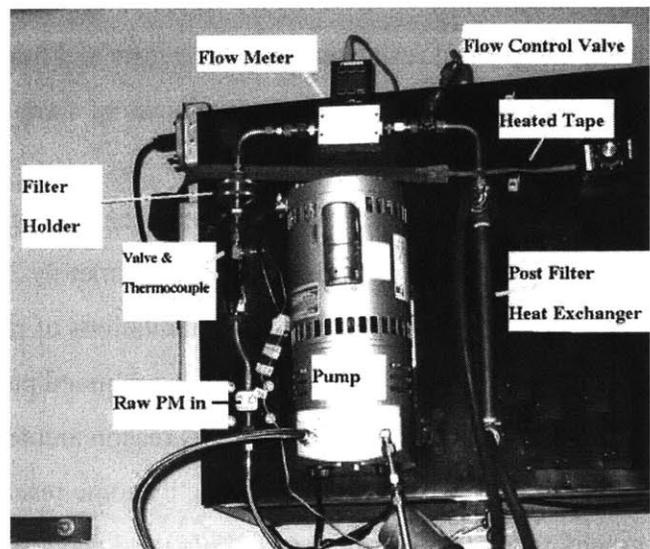


Figure 15 PM emissions sampling system.

exhaust sampled. This data was used to find the average amount sampled for calculation of raw PM accumulation over time based on subsequent gravimetric weighing. To ensure consistency between engine conditions flow rates were reduced to ensure a pre filter temperature of 50-70°C. A tape heater was wrapped around the filter holder and the temperature raised to 80°C to prevent water condensation caused by the attachment of a cool holder to the pre-warmed sampling lines between tests. Another tape heater was used on the raw sampling line to reduce condensation and thermophoresis.

### 2.6.2 Filters

Previous tests on this engine were completed using Pallflex Fiberfilm filters. These filters were chosen for their relative stability in changing temperature and humidity. Filters of this type are recommended by the EPA's own test procedure[86]. Their 96% efficiency rating and fluorocarbon binder make them suitable for EPA testing requirement up to the 2007 regulations. They are unsuitable under EPA 2007 test requirements which dictate the use of PTFE coated filters with 99% efficiency[85]. The EPA test requirement change benefits are demonstrated by several studies carried out on particulate filter characteristics related to temperature, humidity, static charge, and repeatability [26, 28, 87].

Additional filters used in this study included Pallflex Tissuquartz and Pallflex Emfab filters. As a result of the use of all three a parallel study was conducted to observe the effects of experimental and environmental variables on their design. Emfab type PTFE filters reportedly have the greatest resistance to temperature and humidity affects and entrain greater amounts of PM within the membrane reducing losses of sample during movement. These filters were used exclusively for PM measurement.

Analysis of the initial data indicated filters have certain maximum loading capacity. Emfab filters become saturated at approximately 2.5mg. After this amount further accumulation is virtually eliminated. Therefore calculations of raw PM emission in terms of g/kW-hr will be less than the true value if sampling is continued past saturation. Changes in filtering properties also occur at higher loading. For this reason ambient air sampling loading of filter materials has been recommended at less than 1mg by some researchers[88]. Given the approximate .1mg error associated with the gravimetric scale used and the upper bound here sampling times were adjusted to collect between .8mg and 2mg. Samples not in this range were rejected.

Fiberfilm filters were used for comparison to previous studies and for collection of larger amounts of particulate for subsequent TGA analysis. Fiberfilm filters collect greater amounts of particulate matter on the surface providing the opportunity to remove sample carefully. In addition TGA analysis of blank filter material indicates a 25% reduction in mass over the 0% reduction by Tissuquartz, reducing the possible error in ash calculation which can be created by the inadvertent scraping of filter material into a TGA sample. The weight change is consistent with the evaporation of the TFE binder on the filter[89, 90]. Fiberfilm filters have been found more prone to changes in weight due to temperature and humidity as proposed by Brown et al [26]. Fiberfilm filters were also more prone to damage due to higher temperatures and humidity in filter holders which can cause o-ring sticking. This effect was reduced by collecting samples between 50°C and 70°C. Saturation of Fiberfilm filters occurs at approximately 3.5mg. Where these filters were used for collection of raw PM for thermogravimetric analysis they were run past saturation to maximize accumulation.

Tissuquartz filters demonstrated the greatest variance due to temperature and humidity and were the most susceptible to physical damage. They were chosen for their resistance to temperature at 1000°C and their resistance to adsorption of acid gases such as HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. These filters are used in thermal-optical measurement of diesel particulate for the characterization of elemental and organic carbon for the purpose of assessing workplace climate characteristics[91]. These filters are preheated by the manufacturer to remove trace organic components and have an aerosol retention rate of 99%. The quartz is prone to adsorption of organic gases during collection in comparison to PTFE coated filters [27, 92]. Initial tests were conducted on the feasibility of measuring ash from small portions of loaded filter cut using a punch of approximately 12mm<sup>2</sup>, the maximum size which would fit in the TGA pan. Saturation occurs on these filters at 4mg, producing load to filter ratios of approximately 4:100. Thermogravimetric analysis of blank filters revealed no detectable weight loss up to 1000°C. The small percentage of sample to filter, and even smaller percentage of ash to filter, exceeded the limitations of weighing directly using thermogravimetric analysis.

Similar TGA tests on loaded and unloaded Fiberfilm filters revealed filter to load ratios insufficient for accurate analysis on the material. In an isothermal experiment at 600°C a mass loss of 75-77% was noted on the unloaded filter and 76% on a loaded sample. The magnitude of the mass loss and behavior of the unloaded filter indicate significant loss from a filter itself. The

rating of the filter at 315°C suggests that the material is unsuitable for this purpose. Pallflex reported similar behavior of the filter material under heat [90]. The PTFE binder is expected to decompose rapidly at 550°C and be completely decomposed and volatilized in an inert atmosphere at 600°C [89].

Filter flow rate differences had to be accounted for. Tissuquartz and Emfab filters expected flow rates are roughly half those of Fiberfilm filters. Flow rate drops as filters become loaded are therefore faster. Careful observation during early testing allowed determination of flow rates and times which returned filters loaded below saturation at the design collection temperature of 50-70°C. Flow rate duration and rates used are presented in Chapter 3.

Raw PM tests were conducted by loading several Fiberfilm filters and carefully removing sample material from the top of the filter to the TGA pan. Ideally sample mass should exceed 4mg to provide reasonable results.

The microbalance and environmental requirements of 40CFR86 1312-2007 were followed with some exceptions and provisions: temperature and humidity during weighing were recorded in lieu of a strictly controlled environment with corrections made based on control filter data; Aluminum foil on the balance was used to dissipate static charge, a method proven effective in other studies[26]; the number of samples taken was based on past data taken with this test engine, with a minimum number of acceptable samples considered to be three [30]; buoyancy and drift effects were taken into account using a tare control filter technique described in the appendix; filters were pre-conditioned for 48 hours prior to initial weighing and used within 8 hours of that weighing; filters were post-conditioned after loading for approximately 24 hours.

The weight control room temperature and humidity varied  $\pm 5^{\circ}\text{C}$  and 30% RH during the course of the study. Results of control filter tracking showed only minor changes in weight given the temperature and humidity changes recorded during this study which was conducted in spring. Different times of year could produce greater changes on values derived.

Conditioning times are known to affect presence of volatiles in the sample [26], however the conditions in a DPF should can have similar effects. Given this information the overall weighing procedure was devised and is included in Chapter 3 and the appendix.

A detailed uncertainty budget was calculated in accordance with the procedures set forth by NIST[93]. Based on given and measured information during testing the following factors

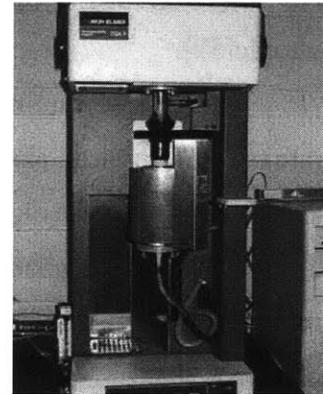
were used for uncertainty calculation: standard deviation of multiple filter weighing before and after test runs; standard deviation of percent of exhaust sampled as measured by engine test apparatus; standard deviation of measured engine output power (KW); combined uncertainties of multiple tests runs. Variation in filter weighing and measurement of engine output power (variation in engine speed and load over test) provided the greatest calculated uncertainties.

## 2.7 Thermogravimetric Analysis

For thermogravimetric analysis a Perkin Elmer TGA7 contracted on a self use basis from MIT's Center for Material Science and Engineering (CMSE) was used. The TGA7 is capable of measuring to the microgram with static and environmental noise adding approximately  $\pm 10$  micrograms. Sample sizes are up to approximately 4 mm in diameter. Calibration of the meter was carried out before tests to ensure accurate temperature control and mass readings over the range specified. To do this Calcium Oxalate and recorded standard curves were used. To ensure accurate

thermogravimetric curves careful calibration and baseline analysis must be carried out. Empty sample pans were run through complete test programs and baseline behavior recorded. It was noted that in general during temperature increases the sample weight also increased proportionately to the scan rate. A similar decrease was noted during cooling. This behavior is consistent with most thermogravimetric analyzers[89]. This information was used to correct raw curves to ensure greater accuracy. Given the small samples used, between .5mg-1.0mg, absence of these corrections created errors in excess of 5%.

The measure of Carbon by thermal techniques is well documented. Discernment of organic carbon from elemental carbon can be carried out using different atmospheres. Organic carbon will volatilize in an inert atmosphere whereas elemental carbon requires oxygen for combustion[94]. A combined gas chromatography, mass spectrometric, and FTIR study could be used to determine the organic compound mixture as well[27], however this was not investigated in this study. Generally inert and helium atmospheres are used to determine elemental and organic atmospheres using thermal-optical techniques.



**Figure 16 Perkin Elmer TGA 7.**

An alternative method for analysis of PM has been presented in various studies. Stratakis et al identified plateaus in diesel soot at approximately 150°C, and 550°C, consistent with the findings of Zinbo et al. In addition the latter study found strong correlation between values for organic fraction (VOF or SOF) obtained using extraction techniques and analyzing thermal curves between 150°C and 380°C in air atmospheres.

Gilot et al conducted a detailed study on thermal kinetics of the soot bed within the thermogravimetric analyzer and determined bed depths of less than 1mm and sample masses of less than 5mg were required to ensure isothermal behavior and proper oxidation of the entire sample[57].

Initial tests on this apparatus also showed a change in purge gas pressure of just 2 psi or rate of 5 mL/min can change the mass reading as much as .01mg. The difference between Air and N<sub>2</sub> did not pose a significant change at a given pressure and flow rate however repeated tests did indicate a slight change of .004mg. This was most likely due to different purge gas regulators.

## 2.8 FTIR Equipment

Some attempts were made to apply FTIR to the analysis. FTIR is commonly applied to used lubricant oil to determine soot and fuel dilution in accordance with ASTM E 2412-04, Standard Practice for Condition Monitoring of Used Lubricants by Trend Analysis Using Fourier Transform Infrared (FT-IR) Spectrometry. It is also used in some thermogravimetric applications and applied to the exhaust gas streams to determine species released during thermal analysis.

Due to the high IR absorbency of Carbon FTIR provides significant challenges for exhaust PM characterization. As such most literature on the subject of exhaust PM characterization is based upon XRD, ATOFMS, and Chromatography, with little information available in regards to FTIR use.

Initial tests using a Nicolet Magna 860 FTIR Spectrometer showed that the absorbency of the borosilicate glass and quartz filters was too high for use in an FTIR microscope or bench.

## 2.9 Raman Equipment

A Kaiser Hololab 5000R Raman Spectrometer with Raman microprobe attachment was available and a raw PM entrained Fiberfilm filter was analyzed to determine applicability to this study. Initial tests indicated that the non reflective nature of PM material prevented good response from the instrument. With additional time and research this may still be a viable method for characterization.

## CHAPTER 3 EXPERIMENTAL DESIGN AND PROCEDURE

### 3.1 Experimental Overview

The previous chapter discusses several of the limitations and assumptions used in designing test procedures, as well as short tests of equipment and calculations used to define test capabilities. These limitations were incorporated into the overall test design for the purpose of providing accurate results. More involved experiments alluding to the characterization of limitations included the Sulfur in oil tests and test of filter material behavior which were carried out in the course of the main experimental test matrix. These are discussed here with results presented in chapter four. Many of the tests, such as filter characterization and accelerated oil consumption rates, were conducted concurrently with these required tests. For instance, during Sulfur in oil tests, oil consumption was calculated and raw PM collected, providing an additional opportunity to examine the effect of using accelerated testing to increase oil consumption. During raw PM collection tests control filters were carefully measured and observed to provide information for future researchers doing similar testing. Experiments involved in this study included:

- Effective Sulfur content in test oils
- Accelerated oil consumption tests
- Oil consumption, SO<sub>2</sub>, and NO<sub>x</sub> mapping in test engine
- Oil consumption vs. emissions tests
- Filter material temperature and humidity sensitivity characterization
- Ash content in fuel and oil tests
- Ash content in raw PM tests

### 3.2 Effective Sulfur Content in Test Oils

Oil composition is frequently proprietary and difficult to obtain. Even when obtained results for a specific batch cannot be accurately assessed without local tests. In addition there are unique difficulties related to sensing SO<sub>2</sub> in exhaust gases as discussed previously. To provide a test method for determining Sulfur content, particularly as it relates to the sensitivity of our test equipment and experimental setup, a method to evaluate Sulfur mass percentage was devised

using the Sulfur Dioxide meter and the test engine. This provided valuable information on the detectability of Sulfur in our designed experiment.

Utilizing the mass balance equations already discussed, a sub program was devised using the existing data acquisition system and engine to use the prime mover as a large Sulfur test system. Using the fuel mass consumption scale a mixture of oil and fuel was made in a lab beaker and supplied to the system. The consumption rate of fuel and oil is therefore known. The use of fuel provides a suitable medium for the engine operation to prevent damage from attempts to burn excessive oil. Increased quantities of non combustibles present in lubricating oils are not intended for engine combustion on a large scale. In this analysis the low Sulfur oil was used as the engine's primary lubricant so the amount of oil Sulfur emitted is extremely small and assumed negligible given the amount generated from the fuel mixture. This assumption was further supported by testing of the oil used in the sump at the time of the test using TGA. TGA results indicated possible fuel or other diluent by determination of a lower ash level than that found in fresh samples of the same product. Hence, Sulfur levels in the low Sulfur oil may have been reduced. As an iterative process later calculations were made including the effect of this lubricant's calculated Sulfur content.

With the fuel/oil ratio and the fuel Sulfur fraction known the amount of Sulfur in the test oil can be determined. Prior to setup an estimate of the air fuel ratio and consumption rates were used from previous tests to determine a suitable oil to fuel ratio to provide a level of SO<sub>2</sub> within the range of our analyzer. For simplification in calculation and programming the ratio of dry exhaust to wet exhaust is assumed that of the stoichiometric ratio of FT fuel. Fuel consumption for this blend was measured and found to be the same as that experienced when using straight FT fuel.

The equation for determining Sulfur content based on the above derivation follows. The second term takes into the account the actual oil consumption of that oil circulating within the engine in normal operation. Since low Sulfur oil was used, the effect of this should be negligible in comparison to the large amounts consumed in the blend. For lower percentages of oil doping this figure becomes more important. This value was assumed in calculation to be equal to that value later determined using high Sulfur oil which is assumed to be a conservative estimate. Given the small amounts involved this iterative term could be assumed zero.

$$\xi_{s,o} = \frac{\xi_{s,we} * \dot{m}_{w,e} - \xi_{s,f} * (1 - \xi_{o,b}) * \dot{m}_b}{\xi_{o,b} * \dot{m}_b} - \xi_{s,o} * \dot{m}_o$$

$\xi_{o,b}$  = mass fraction oil in fuel/oil blend       $\dot{m}_b$  = mass flow of fuel oil blend consumed

This test was conducted at two different engine conditions using new samples of both oils. Concentrations were also varied to determine possible effects of doping induced errors to this calculation. During operations several beakers of the mixture were made and burned almost to the bottom with excellent repeatability amongst tests. This suggests mixing of oil in fuel was even and the mixing composition was kept relatively constant.

**Table 7 Effective Sulfur in Oil Test Matrix**

Test Condition	Oil Sulfur	Mass Fraction Oil in blend	Expected $\xi_{s,we}$ (ppm <sub>v</sub> SO <sub>2</sub> )	Approx. Oil Consumed (g/hr)
I25	Low	.02500	5	77
I25	High	.01250	5	39
A50	High	.00625	5	102
A50	High	.00200	1	36

### 3.3 Accelerated Oil Consumption Tests

During the estimation of Sulfur in oil tests raw PM was collected on particulate filters in accordance with the main test matrix procedure as discussed in section 3.5. The mass of oil consumed as a function of the fuel consumption rate measured is given in the table above. Actual calculations of expected ash were derived using this value in addition to the estimated oil consumption from later tests.

### 3.4 Oil Consumption, SO<sub>2</sub>, and NO<sub>x</sub> Mapping

The Sulfur Dioxide analyzer was used to map oil consumption over the entire engine operating range. This was the first estimate of oil consumption on this test engine and was conducted using the high Sulfur oil. Both speed and load were varied in accordance with the test matrix below. Condition A50 (1680 RPM) is included as it was part of the main test matrix for raw PM and ash collection as described in section 3.5. Engine operation and use of analyzers

were in accordance with the test procedure presented in section 3.5 and results from these tests were compared where tests overlapped to ensure repeatability. Given the frequent engine condition changes spanning of the instrument was conducted prior to each engine condition tested. Careful spanning and calibration took approximately 30 minutes to pass through zero air, Sulfur Dioxide span gas, three NO span gases, and await the settling of temperatures in the upper box of the analyzer. Maximum variation of oil consumption was expected between low speed and load and high speed and load.

The Sulfur mass fraction in the test oil used was 1.3% as determined by the effective Sulfur in oil tests conducted previously. This value is considerably lower than the 2.03% given by the manufacturer, reasons for which are presented in Chapter 4. Use of the higher mass fraction of Sulfur would result in a linear decrease in calculated oil consumed.

The O<sub>2</sub> level was reduced during this test as discussed in Chapter 2. As these tests were run after the oil consumption vs. emissions generation tests the effect of reducing O<sub>2</sub> was compared to the values for lube oil consumption from those tests and found to be comparable as predicted in Chapter 2.

The test matrix used for mapping:

**Table 8 Test matrix for lube oil consumption mapping.**

<b>Engine Speed (RPM)</b>	<b>Engine Load (% rated)</b>
750 (idle)	0, 25, 50, 75, 90
1000	0, 25, 50, 75, 90
1500	0, 25, 50, 75, 90
1680	50
2000	0, 25, 50, 75, 90
2500	0, 25, 50, 75

### 3.5 Oil Consumption Effect on Emissions Tests

A test matrix was devised based on the limitations of the testing equipment, the interest of gaining an elementary understanding of the mass balance of ash and its relation to oil consumption, on known oil consumption mechanisms, and on past tests run on this engine. These tests constituted the core of the study data.

The test conditions chosen were intended to cover a broad range of engine conditions. 75% load was tested to prevent excessive wear on the test engine for preliminary tests. 25% load

tests were conducted as opposed to 0% load to have some small load on the test engine. Previous researchers using this engine based studies on the European Stationary Cycle as outlined in the Euro-III directive of October 2000. Previous test conditions studied extensively on this engine were chosen for high PM production rates. The previous conditions were A25, A50, B50, and B75. The letter designation pertains to the speed in the test cycle, calculated for this engine at 1680 RPM for “A”, 2000 RPM for “B”, and 2345 for “C”. The 1000 RPM condition was chosen as a near idle condition for observance of low speed, low load conditions and may be designated at times in this report as condition speed “I”. Number designations correspond to percentage of maximum rated load at the given speed. Test condition A50 was chosen as the center point due to its use in several previous studies conducted on emissions using FT and low Sulfur fuels[30, 52]. Data from these past tests provided valuable baseline information for comparison to initial results using the low Sulfur oil. The overall test matrix is presented in tabular form below.

Previous studies on this test engine included a detailed study of different fuel Sulfur content, EGR, and ignition timing effects on NO<sub>x</sub> and PM emission. In some of these tests raw exhaust samples were also collected. As explained previously other tests were conducted on equipment added to the test engine including temperature and electrical drift effects on the SO<sub>2</sub> analyzer, NO<sub>x</sub> interference with the SO<sub>2</sub> analyzer, effect of filter media on PM sampling repeatability, effect of temperature on particulate filter flow rate, and effect of temperature and humidity on filter weight analysis.

Filter flow rates were controlled to ensure similar temperatures of collection and overall proper mass accumulation. Observation of early studies indicated the following collection rates were optimal for the given lab configuration. Flow rates and times are given for Emfab filters which were used for raw PM accumulation calculation and Fiberfilm and Tissuquartz filters which were loaded to saturation for future TGA testing. Unfortunately initial samples were not collected past saturation, preventing ash analysis of some low Sulfur oil conditions. As such collection times were revised and are presented below. Different pumps and sampling systems will obviously require different rates and times.

**Table 9 Engine emission test matrix collection times and flowrates**

Speed (RPM)	Load (%)	Emfab		Fiberfilm, Tissuquartz	
		Flow rate (LPM)	Time (min)	Flow rate (LPM)	Time (min)
1000	25	180	8	180	60
1000	75	180	15	180	60
1680	50	180	4	180	10
2000	25	180	5	180	20
2000	75	180	5	180	20
2345	75	180	5	180	15

Sulfur Dioxide readings were taken during all conditions. Detectable limits were not discovered while using FT fuel and low Sulfur oil during normal operating conditions as expected by initial assumptions of a <.5% Sulfur concentration in the lubricant.

The overall test procedure for engine operation is detailed in Appendix A and defines the evolution of steps from running of the engine between filter pre and post weighing. Procedures and shakedown results described in detail in other sections of the report are excluded for brevity. Weighing procedures are included in a following section.

### 3.6 Filter Temperature, Humidity, and Weighing Procedure Effects Tests

To test filter resilience and provide a relative comparison of data collected in studies using different filters and those conducted previously on this engine a test matrix was formed using the three different filter types. These were run at engine test condition A50 for which previous studies had already been completed using FT fuel and low Sulfur oil. Tests were run at 5 minutes each as had the tests in the previous studies by Acar[30].

Additional tests involving filters were also part of this study. The mass handling procedure chosen was based on the information gained in the above research. The procedure is derived from EPA requirements[85], past results from tests on the subject engine[30], and various studies regarding the effects of filter material and ambient conditions[26, 28, 87]. The detailed mass handling procedure is contained in Appendix A.

Relative humidity and temperature variation was limited during this study given the time of year, however some fluctuations in control filter mass were noted.

### 3.7 Ash Content in Fuel and Oil Tests

As discussed several methods exist to characterize petroleum products in terms of volatiles and ash. Tests were conducted on fluids here to determine potential behavior during transport through the engine and exhaust system. The test programs chosen were based on the information provided in the standards described previously. While the standards all address the issue of ash and volatiles, they differ slightly in terms of recommended atmospheres and specific temperatures depending on their primary focus. In general ash is considered to exist above 750-775°C and volatiles will combust between 120-200°C. Steps were added to include the 600°C isothermal hold given the definitions of trap ash discussed earlier. In accordance with the standards an inert atmosphere was used until 650°C for some tests.

FT fuel and new and used oil samples were evaluated using the general program listed in appendix A. Isothermal holds were used for initial tests for experimental purposes and then reduced for most studies as no discernable plateau was recognized during these long holds, suggesting slow combustion of products in the inert atmosphere. The 150°C recording is recommended as the agreed upon point to estimate the mass percentage of high volatiles including water[22, 38, 39, 44, 45]. The atmosphere and subsequent heating between 650°C and 750° is set forth in ASTM D5967 as the recommended step defining soot concentration in used lubricants. For new fuel and oil this soot step was not required. Temperatures of 775°C and above generally pertain to ash products with potential existing for slow decomposition over long periods of time in some cases requiring an agreed upon point for estimation[38]. While ASTM E 2403 requires 60 minutes at elevated temperatures to determine sulfated ash it was found that plateaus were stable for simple ash estimation (i.e.- Sulfuric Acid omitted) after only 5-10 minutes. The program in the appendix allows for comparison of volatiles, soot contamination, and ash.

### 3.8 Ash and VOF Content in Particulate Matter Tests

A TGA analysis was conducted on the raw PM in a manner similar to that set forth in ASTM standard E1131-03, Standard Test Method for Compositional Analysis by Thermogravimetry[38]. The standard requires introduction of an inert gas and air into the combustion atmosphere. While not exact this method provides a representation of the exhaust laden atmospheres present in a trap during regeneration. Diesel exhausts on an engine of this type with relative A/F ratios in excess of two produce lean exhaust gas mixtures which should have sufficient amounts of O<sub>2</sub> to provide combustion for trap PM. The percentage of O<sub>2</sub> in the exhaust stream over the range of operations is approximately 11% to 18%, greater than half that present in the ambient atmosphere. Air added to the TGA during analysis in this test was a combination of N<sub>2</sub> for system purge gas and approximately 20 ml/min of zero grade air, reducing the O<sub>2</sub> content to near exhaust system levels. Another significant component of exhaust gases not present in this mixture is H<sub>2</sub>O which would likely have a cooling effect on combustion characteristics during trap regeneration. Specific steps of the TGA program are discussed in the appendix.

For raw PM analysis an air atmosphere was used throughout the test in a manner similar to that presented by Stratakis et al and Zinbo et al [44, 45, 53, 55]. Using this method the volatile organic fraction (VOF) can be derived directly in the thermogravimetric curve as the loss between 150°C and 380°C. The majority of VOF is believed to be from lubricant, making this the most direct estimate of lubricant impact on particulate matter and soot[22]. Fuel derived VOF is composed of lighter species. Based on tests conducted on fuel and lubricants in the last section it is evident that the FT fuel used contains much lighter species than the heavier lubricants, with most of the mass evaporated by 150°C. Given the impact of high exhaust temperatures and the long exhaust tailpipe present on the test engine it is likely that an even greater majority of VOF in the PM collected is lubricant derived.

Samples were chosen for analysis based on the amount of raw PM collected and the relative oil consumption expected at the condition. Given filter loading times presented earlier it was found 1 to 2 filters were required to remove sufficient sample masses of .5-1.0 mg for analysis. Smaller samples increased error considerably in relation to analyzer limitations. Larger

samples were not used to avoid non-isothermal heating and oxidation given the small pan size used. The test program used is detailed in appendix A.

Temperature corrections can remove the need for long cooling times if confidence exists that the baseline is accurate. For most samples cooling was continued to room temperature to ensure proper estimation of baseline temperature effects. In addition the 800°C isothermal hold was continued for 30 minutes for initial samples. Plateaus were stable and little variation was found in mass percentage over 5 minutes in this program step and it was reduced for later samples.

## CHAPTER 4 RESULTS AND ANALYSIS

### 4.1 Effective Sulfur Content in Test Oils

#### 4.1.1 Anticipated Results

Results of ASTM D4294 were available from the manufacturer to define the Sulfur content of the high Sulfur oil. Similar recovery rates were expected. Sulfur content of the low Sulfur oil was not known leading to the initial motivation for this test. The low Sulfur oil was expected to have a Sulfur content of approximately .5%.

#### 4.1.2 Actual Results

Actual results differed significantly from expected as shown for the high Sulfur oil tests. Doped fuel was mixed and run for over thirty minutes for each study with the test beaker filled and near drained several times with no concentration effects from improper mixing noticed. The Sulfur level of 1.3-1.4% measured is 65-70% of the 2.0% expected. Results were consistent to within  $\pm 1$  % Sulfur for the entire length of tests.

Two separate sampling ports were used with no change in results. Both were approximately 10 pipe diameters downstream of the exhaust tailpipe inlet, with the second containing approximately 6 inches more stainless steel tubing than the first. It is possible that some of the error is due to suction of the sampling system of lighter species from the exhaust, potentially excluding heavier raw PM and ash containing Sulfur.

The most likely cause is absorbance in the sampling system as discussed earlier, particularly in internal stainless steel tubing and fittings within the meter which can rise to temperatures as high as furnace set points of 1000°C. This theory is confirmed by the work of Lizumi[23]. In this study decreases of expected Sulfur of 20% were realized using a stainless steel furnace as compared to a quartz furnace. Adsorption in EGR and turbocharger components is also possible.

An additional cause of reduced rates is the sulfating of PM during combustion and within the exhaust. Sulfur is known to adhere to metallic particulate to form ash, leading to the quantification of sulfated ash as discussed earlier[38]. Metallic ash and non combusted PM may be held by glass fiber in the two furnaces and not allowed to react with O<sub>2</sub>.

Test conditions and doping levels were varied to rule out the possibility of error from low temperatures at the I25 condition or high doping rates used. Results were remarkably similar

across all testing conditions. Lizumi et al showed an increase in adsorbance with increased Sulfur Dioxide present[23]. This effect was confirmed by comparison of the .2%<sub>wt</sub> vs. .6%<sub>wt</sub> doping conditions. Calculated Sulfur fraction in the first case was 1.4%<sub>wt</sub> for the first condition vs 1.3%<sub>wt</sub> for the latter, confirming an increased adsorption of SO<sub>2</sub> for the higher doping condition. A greater decrease in measured Sulfur concentration is realized if the effects of normal operating lubricant consumption are factored into the results. Estimates of low Sulfur oil consumption based on later high Sulfur oil tests in an iterative calculation show that these effects are more significant for the low doping condition, with oil consumption of the low Sulfur oil from the sump being a larger fraction of the overall Sulfur content in the exhaust in the .2%<sub>wt</sub> vs. .6%<sub>wt</sub> doping condition tested.

In accordance with these results a Sulfur concentration of 1.3% was used for actual lube oil consumption calculations in later engine tests with high Sulfur oil in the sump. The assumption of Sulfur concentration of the test oil is critical to the magnitude of oil consumption estimated. Higher assumed concentrations will result in a lower lube oil consumption calculated. The 1.3% estimate may be low, as actual lubricant consumption will create lower Sulfur Dioxide production in the exhaust and reduced adsorption.

In light of the high Sulfur oil test and assuming a 30% adsorption correction the actual Sulfur concentration of the low Sulfur oil is estimated at .42%. This is consistent with typical engine lubricants found commercially and with the lack of detection of Sulfur in the exhaust stream when FT fuel and low Sulfur oil are used.

#### 4.2 Accelerated Oil Consumption Tests

During the course of testing for Sulfur in the test oils particulate filters and other emissions data were gathered to determine the effects of doping oil directly into fuel to increase oil consumption. Doping of oil to increase consumption for testing purposes has been well documented in literature and is generally done at low rates of approximately .2%<sub>wt</sub> of the fuel mixture [16, 95]. Doping has also been conducted through use of separate nozzles within the cylinder to increase oil spray patterns and reduce adverse affects on the engine fueling system from increased contaminants[46].

Doping has been found to have an affect on particulate size, with increasing numbers of small particles found in exhausts created by oil doped fuels for accelerated tests[95]. In those

tests, reported by Kyto et al, particulate matter was found to increase considerably if an aged lubricant was used vice a new one. The particle size findings are consistent with those presented by Okada et al who showed increased organic Carbon content and smaller particle size as a results of increased lube oil consumption contribution to particulate[17]. The increase in PM produced by doped used lubricants vice new lubricants is not completely due to entrained soot in the used medium. Entrained soot can measure as much as .5% of used lubricant as confirmed in tests detailed here in section 4.6. If lubricant is responsible for 25% of the total PM then this small amount of soot does not account for the complete increase. During doping tests in this study only new oil was used. Used oil was present in the sump for low Sulfur tests.

The following figure shows the raw PM emissions resulting from the doping of fuel. Considerably higher levels of particulate are produced when oil is doped into fuel at greater than .2% wt was indicated. The high Sulfur oil demonstrated a disproportionate increase in raw PM over the low Sulfur oil which was doped at considerably higher levels to provide increased Sulfur Dioxide responses in the exhaust. The lower volatility of the high Sulfur oil is a likely cause as it should provide for increased heavy hydrocarbons and a greater unburned fraction in the cylinder. Tests using .2%<sub>wt</sub> doping of fuel showed similar results to those obtained with no doping. .6%<sub>wt</sub> doping caused a significant increase in raw PM emissions, with an increase of over 150%. Later tests of oil consumption, reported in section 4.3, suggest the low volatility of the oil requires considerable liner temperatures to induce evaporation in the cylinder. As such the low cylinder and exhaust temperatures present in engine conditions used for doping experiments would support the theory of incomplete combustion of oils leading to greater PM production. The 300% increase in oil consumption in the tests at 1680 RPM led to a 150% increase in raw PM formation. This phenomenon is not seen in undoped tests in which engine oil consumption increases threefold. This suggests the normal mechanisms leading to PM formation from fuels are disproportionately influenced by high level oil doping.

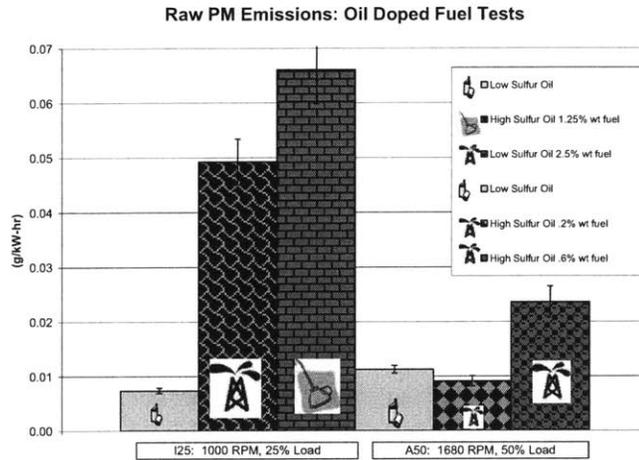


Figure 17 Raw PM emission during accelerated oil consumption tests. (Included in Appendix C)

Analysis of NO concentrations in the exhaust taken throughout testing show no significant changes when doped fuel is used. Slightly lower NO concentrations measured during doping tests for the low speed/low load condition could be attributable to decreases in combustion temperatures due to use of the lower volatile fluids. Cylinder exhaust temperatures did not show significant changes between tests.

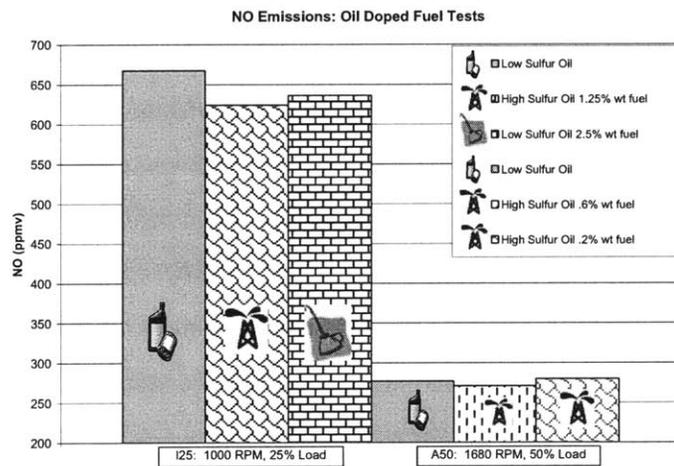


Figure 18 NO emissions during accelerated oil consumption tests

#### 4.3 Oil Consumption, SO<sub>2</sub>, and NO<sub>x</sub> Mapping

Results of Sulfur Dioxide concentration in the exhaust are shown here for the high Sulfur oil. Tests using low Sulfur oil indicated SO<sub>2</sub> responses of 0 ppm<sub>v</sub> (below the lower detection

limit) as expected. At the .35-.42% Sulfur fraction expected in the low Sulfur oil responses even with the expected lube oil consumption rates presented in Chapter 2 would produce values that were half of the lower detection limit of the analyzer.

Since the high Sulfur oil is a commercial lubricant these results indicate the use of an oil with excessive Sulfur can negate the advantages of lowering fuel Sulfur levels. The plot below indicates the “equivalent fuel” condition. At maximum speed and load SO<sub>2</sub> levels in the exhaust from this lubricant contributed an equivalent of 13 ppm<sub>w</sub> fuel based on calculated fuel consumption for this engine.

Transient effects were not studied, however qualitative observations between test conditions indicate that rapid increases during changes may be an effect of meter drift and not oil pooling as proposed in some studies.

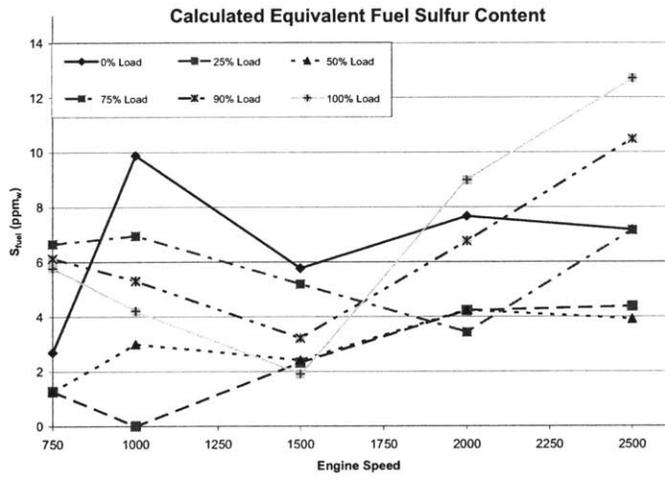
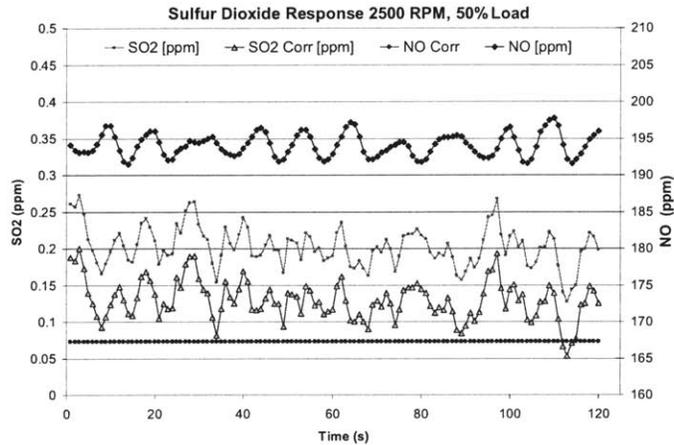


Figure 19 Calculated equivalent fuel Sulfur content. (Included in Appendix C)

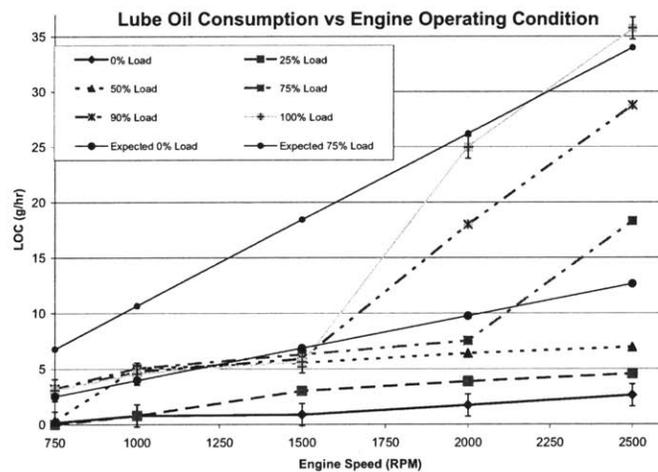
At steady state rates SO<sub>2</sub> levels remain relatively constant, with excellent repeatability between tests on separate days. Typical test runs consisted of sampling for several minutes while particulate filters were loading. As discussed in the data acquisition section the detector module for the analyzer returns three sample readings per second. To ensure elimination of noise the data acquisition system captured and averaged 100 samples per second, providing 60 data points per minute. Standard deviations of SO<sub>2</sub> emission were calculated for each test run and ranged from 10-20% of the average response. Given the small responses involved, on the order of ppb<sub>v</sub> SO<sub>2</sub>, much of this variation is expected to be DAQ noise and is therefore canceled by curve smoothing. The response curve for a two minute test run is shown below. The right axis

corresponds to the top curve representing ppm<sub>v</sub> NO. The next curve is the raw SO<sub>2</sub> response, followed by the corrected SO<sub>2</sub> response and the NO correction which is the SO<sub>2</sub> response attributed to the NO.



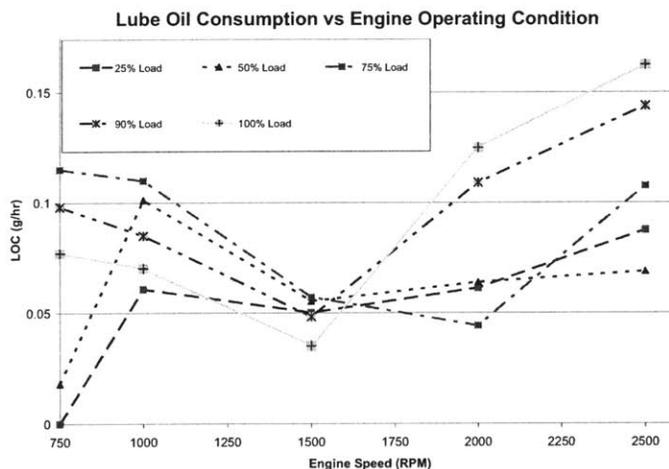
**Figure 20 Sulfur Dioxide detector response and NO corrections for steady state condition. (Included in Appendix C)**

Results of lubricant consumption are a multiple of those of SO<sub>2</sub> given the majority contribution of Sulfur is from oil. With a Sulfur content in fuel of only 90ppb<sub>w</sub> the effect of fuel, while calculated, negligible. The figure below shows the measured lube oil consumption over the entire operating range of the engine. Standard deviations of 1-2 g/hr were calculated at each test condition over the duration of test runs.



**Figure 21 Measured lube oil consumption vs. engine conditions. Uncertainty levels indicated for 0% and 100% load are typical for all those measured. (Included in Appendix C)**

The expected lube oil consumption presented in Chapter 2 is also included for comparison. Results indicate that for this engine lubricant consumption is not linear over the entire speed and load range. In addition a significant increase in relative lubricant consumption is seen between 75% and 90% load over the entire speed range. This could be for a variety of reasons. The most likely cause is increased liner temperatures at the higher loads. Consumption of low volatility oils has been found to be greatest with high liner temperatures[12]. The oil used was formulated by the manufacturer for high film thickness and volatility, which is consistent with this effect.



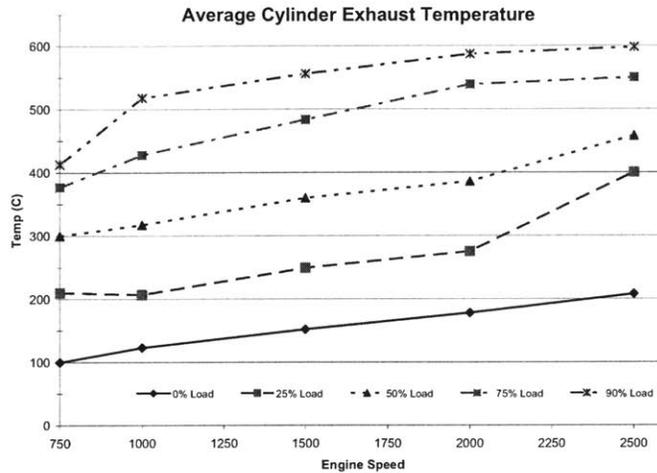
**Figure 22 Measured lube oil consumption vs. engine conditions in g/kW-hr. (Included in Appendix C)**

Maximum oil consumption was found to be less than the expected consumption model used however it was within the range of consumption expected for an engine of this size. Adsorption effects were already accounted for by the use of a lower than expected Sulfur fraction as discussed in section 4.2. High oil volatility and film thickness are likely reasons for the reduced consumption at lower operating speeds where cylinder liner temperatures are lower, however further studies with different lubricants would be required to confirm this. Comparing average cylinder exhaust temperatures (see figure below) to the oil consumption reveals significant increases in oil consumption are related to cylinder exhaust temperatures over 400°C. TGA tests of the lubricant oils, discussed in a following section, indicate a significant increase in oil evaporation at approximately 400°C. Liner and in cylinder combustion temperatures are likely much higher than exhaust temperatures. Oil transported through the cylinder yet not combusted may be more likely to condense on or remain in the cylinder after combustion with lower exhaust

temperatures. Hence, exhaust temperatures over 400°C are expected to keep evaporated oil in a gaseous state for transport out of the cylinder. Engine oil sump temperatures showed similar trends however only varied between 85°C and 105°C over the range of operating conditions.

Conditions of the test engine are also a source of variations between measured results and those of engines discussed in literature. Specific design considerations in relation to ring behavior and wear can have a significant impact on oil consumption.

Additional studies of Sulfur concentration over the oils distillation range are required to confirm that oil Sulfur concentrations used are accurate. Studies have shown that Sulfur concentration may not be constant over the entire distillation range, generally with Sulfur existing in the lighter species of the oil[12]. Yilmaz used model predictions to show that the first 6% of the oil distillation curve representing volatile species accounted for 80% of evaporated oil in the cylinder, with species in the first 40% of the curve contributing to 95% of oil evaporated[12]. This suggests the overall error attained by as much as a 50% change in Sulfur content over the entire distillation range of an oil will have limited impact on the method parameters assumed here. This is particularly evident in the fact that oil consumption predictions are lower than expected in this study. Generally, oil Sulfur levels will be higher in the more highly volatile species of an oil, resulting in an overall higher prediction of oil consumption if the average content is used. In addition low values for oil consumption calculated suggest the use of the lesser Sulfur fraction in oil as discussed in section 4.1 are justified. Had the original 2% Sulfur fraction been used for calculation oil consumption calculated would be lower by an additional 20-30%.



**Figure 23 Average cylinder exhaust temperature variation. (Included in Appendix C)**

NO<sub>x</sub> concentrations did not vary significantly changes between oils used. Any changes indicated are likely due to fluctuations between testing days and experimental error.

Comparison of power output between the test runs with the two oils indicate a slight increase in power output for given speeds consistent with claims of 3% power increase made by the oil manufacturer. These tests are not conclusive as the increases fall within the uncertainty of the engine instrumentation and the power output changes were not a focus of these studies. These results are only included as an interesting sidebar. Pressure trace analysis of heat release rates of FT fuels were conducted by Sappok using both oils in the system. The oil created no change in pressure trace data for the engine conditions studied[31].

#### 4.4 Oil Consumption Effects on Raw PM Emissions Tests

Raw PM results are shown in figure 24. As indicated a slight increase in raw PM was shown for the high Sulfur oil at the chosen test conditions, however this difference tended to fall within one standard deviation of the average of calculated emission rates. The chart shown includes error bars representing the combined uncertainty calculated for the tests. The uncertainties used included the uncertainty for time of run ( $\pm 1$ s), ratio of sampling flow to total exhaust (standard deviation calculated during runs), calculated power output (standard deviation of KW), and filter weight (based on combined standard deviations from multiple weighing of filters before and after loading). Trends between engine operating conditions were consistent for each oil used. To confirm results more samples may reduce the high relative uncertainty. Values

for raw PM rates using the low Sulfur oil are consistent with past studies on this engine by previous researchers[30]. As discussed in the oil consumption section the chemistries of the two oils may be sufficiently different to cause increased oil consumption in the low Sulfur oil on account of lower viscosity and volatility. This would tend to decrease the difference in expected raw PM emissions rates. Similar levels of volatile organic fraction in raw PM samples calculated during TGA tests indicate that oil consumption between the two oils is likely similar.

Work at MIT by Acar and Sappok produced results indicating an approximate 25% increase in PM generated by 15 ppm<sub>w</sub> fuel vice FT fuel. Assuming a conservative contribution of 25% of that particulate from oil consumption, and the sole mechanism of increase based on Sulfur effects, the addition of 15ppm<sub>w</sub> Sulfur in fuel contributes to a 33% increase in PM. At the test conditions investigated equivalent fuel Sulfur from oil consumption is only 3-4 ppm<sub>w</sub>. Based on this the 10-30% increases in PM measured with high Sulfur oil may be largely due to increased sulfate levels. Ash results presented later indicate 3-5% increases in PM can be attributed to increased ash levels from the high Sulfur oil.

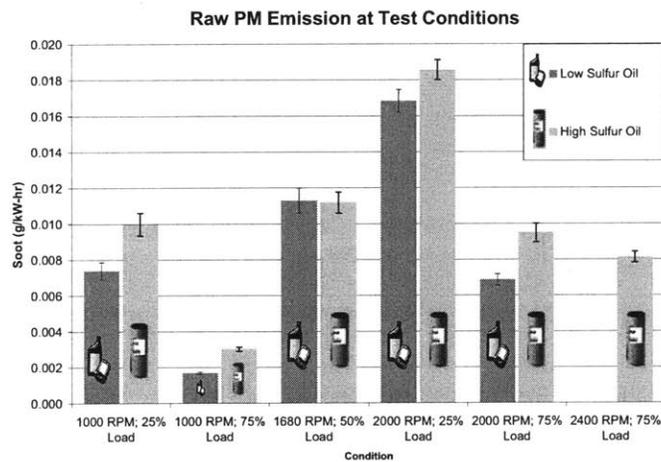


Figure 24 Raw PM emission for varying test conditions and oils. (Included in Appendix C)

#### 4.5 Filter Temperature, Humidity, and Weighing Procedure Effects Tests

Qualitative observations of the different filters used were consistent with those in literature, with Emfab type filters considerably more resilient to testing conditions than the other types. Likewise Tissuquartz type filters were considerably less resistant to structural damage.

Relative humidity fluctuations of only 30% were observed during the duration of testing. Plots below show the changes in control filter weights over intervals measured. Changes in temperature, relative humidity, and length of time in days are indicated for each interval in the first plot. Intervals consisted of 1-4 days. Given the relative low temperature and humidity fluctuations it can be seen that balance and other experimental effects are the likely causes for uncertainty. Of greater interest is the effect of petri dish use during weighing. Traditional procedures for filter weighing in this lab have consisted of weighing filters in petri dishes before and after testing. Trends show that this significantly increases errors in recorded mass, with these errors carrying through to filter measurements. As such overall raw PM emission rates calculated by weighing filters separately were statistically lower than those calculated weighing filters in dishes. In addition to the plots shown, tare filters, loaded filters, and additional control filters followed the same trends. This suggests differences did not result from PM losses during filter removal from dishes or weight increases in the test cell area. Observations of filter behavior indicate static is the primary cause of petri dish induced fluctuations. Relative differences in magnitude of mass could also contribute to drift effects, with petri dish mass exceeding that of the individual filters by over 8000%. Changes in recorded mass of the control weight, which was of similar mass to the petri dishes, supports this theory.

The data also shows that differences between Emfab and Fiberfilm filters are similar in the range of conditions measured. Tissuquartz filters demonstrated greater variability over the first three intervals. Intervals four and five did not include Tissuquartz tests. A small piece of steel weighing approximately 11g, about 120% of the mass of a petri dish, was used as a control weight. Variations in this mass are likely due to scale drift effects from day to day. Results indicate this drift is as significant as filter drift over the range studied.

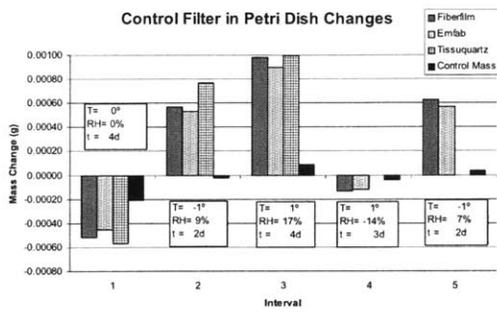


Figure 25 Control filter changes, weighed in petri dish. Change in temperature, humidity, and time included.

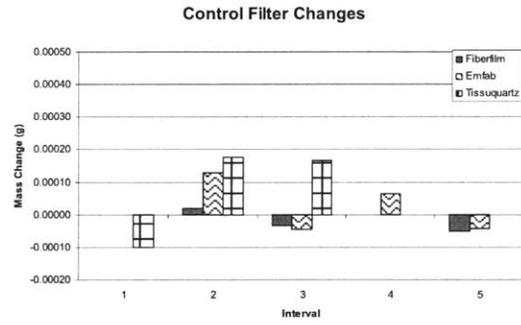


Figure 26 Control filter changes. Intervals are the same as those in previous figure.

PM emission results calculated using the Fiberfilm and Emfab filters at one engine condition were equal within the limits of experimental uncertainty. This supports the use of data comparisons between this and past and future studies on the test engine.

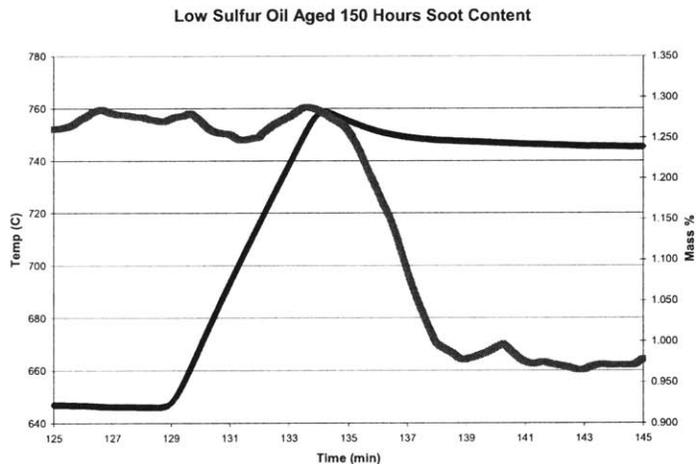
#### 4.6 Ash Content in Fuel and Oil Tests

The ash content as measured in the oils and FT fuel is listed below along with fractions at 150°C for estimate of volatiles. The TGA method showed good repeatability with samples of 15-25 mg.

**Table 10 Results of Lubricant TGA Tests Using ASTM Standard E-1131**

Product	Reported Sulfated Ash <sup>4</sup> % <sub>wt</sub>	High Volatiles (150°C) % <sub>wt</sub>	Medium Volatiles (400°C) % <sub>wt</sub>	Medium Volatiles (600°C) % <sub>wt</sub>	Soot Content (650-750°C) % <sub>wt</sub>	Ash (800°C) % <sub>wt</sub>
Low Sulfur- Unused	1.0	1.5	95	98.5	0.0	1.10
Low Sulfur- Aged 150+ hours	1.0	0.5	95	98.0	0.3	0.85
High Sulfur- Unused	1.8	1.0	96	98.5	0.1	1.65
High Sulfur- Used 100+ hours	1.8	1.0	96	98.5	0.2	1.35
FT Fuel	<0.001	85.0	>99.99	>99.99	<0.01	<.01%

Combustion of soot in oil in accordance with ASTM D5967 showed a .3%<sub>wt</sub> soot accumulation in the low Sulfur oil when it was tested (see figure below). A .1%<sub>wt</sub> soot accumulation in the high Sulfur oil is likely due to decreased aging time in addition to oil composition differences.



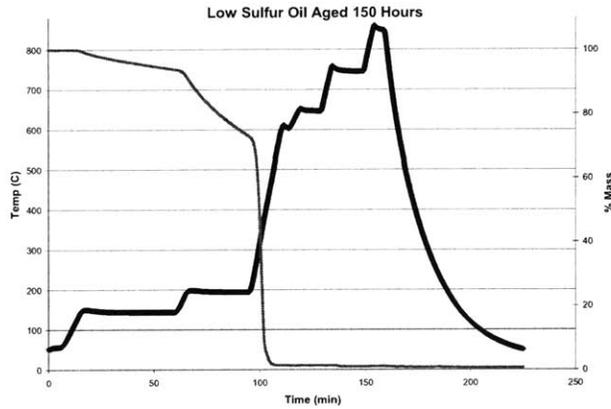
**Figure 27 Soot content in used low Sulfur oil based on ASTM D5967**

<sup>4</sup> Sulfated ash is a standard measured for lubricants. The value given for FT fuel is the upper limit value for ash. Typically ash levels for FT fuel are below this concentration.

The lower ash content measured for both used oils is unexpected given the sooting over time. As the new oil came from the same batch and container as that supplied to the engine composition should be the same. Fuel dilution in the oil is a possible cause of the decreased relative ash content of the old oil, however the test engine incorporates external fuel lines making this unlikely. Coolant dilution is another possibility. The reduced ash level suggests that aged oil may actually cause reduced levels of ash emission over new oils in some cases. In addition, use of aged oil in Sulfur Dioxide testing could lead to errors given potentially reduced Sulfur content brought about by dilution.

Mass percentage decrease at 150°C gives an indication of highly volatile content as suggested by ASTM 1131[38]. Prolonged isothermal holds on the oil at 150°C and 200°C indicate a gradual rate of decomposition of medium volatiles, with rate increasing with temperature as expected. The figure below shows a TGA curve for used oil in this range. As can be seen decomposition continues without an obvious plateau, requiring the need for definition of a standard marker for high volatiles if no plateau exists. Similarly previous studies on raw PM in literature have used a 10°C/min temperature scan and marked the VOF range at 150°C-380°C[54]. As shown in the figure below the percentage of mass consumed by this point in the test oils was less than .5%. Given time for reaction the rate of decomposition increased as shown. At standard rates medium volatiles were combusted at approximately 200°C, 400°C, and 550°C for FT fuel, lube oil, and diesel raw PM respectively.

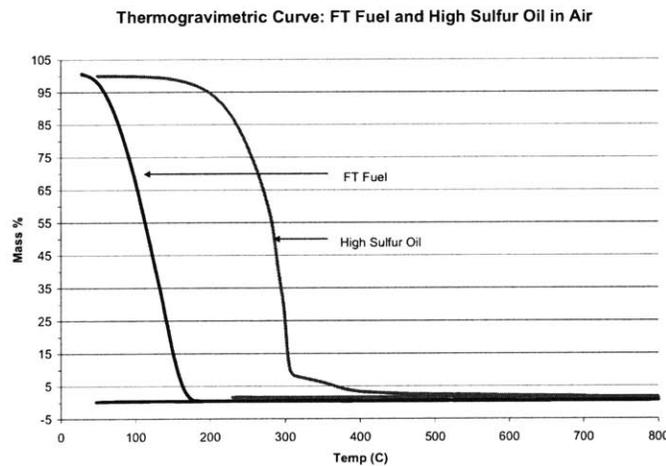
The complete curve of the used low Sulfur oil is shown here. Considerable time was allowed for combustion at different steps in this test as opposed to other tests to show the effect of prolonged isothermal holds. Baseline corrections have been applied. Zero drift for all tests was at most .03 mg. While not evident at the resolution shown here significant increases or decreases in mass readings are possible, with errors correlating directly with the temperature curve.



**Figure 28** TGA plot showing entire curve for aged low Sulfur oil. Temperature is plotted along with mass percentage to show rate effects as well as temperature effects.

FT fuel showed considerably greater volatility as expected. This suggests most unburned fuel hydrocarbons will likely combust in high exhaust temperatures when oil derived hydrocarbons may persist and form on particulate.

The following curve depicting new high Sulfur oil in an air atmosphere calculates the ash percentage of the oil without the addition of Sulfuric acid (as done with Sulfated Ash tests). The curve also shows the near complete combustion at the 400°C plateau. By contrast FT fuel is almost completely volatilized by 150°C-200°C. This supports the theory used previously which attributes the diesel raw PM curve decomposition from 150°C-400°C as the measure of the VOF, generally associated with oil consumption. Similar behavior is seen in decomposition in an inert atmosphere, with slower decomposition rates causing a slightly higher percentage of mass remaining at the 400°C index.



**Figure 29** Volatile concentration estimate in FT fuel and oil using air atmosphere

## 4.7 Ash Content in Raw PM Tests

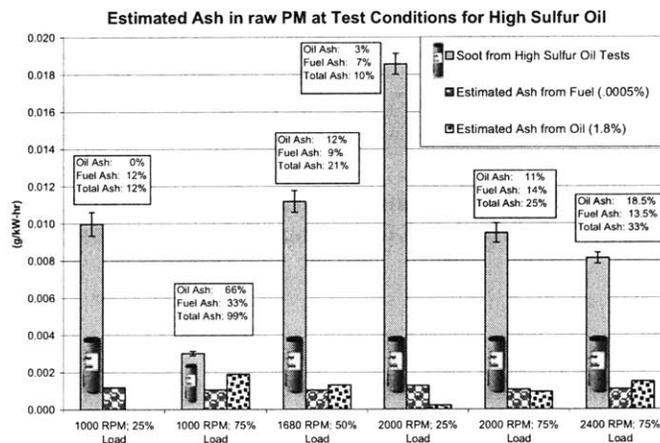
### 4.7.1 Anticipated Results

VOF levels in literature, for example Sharp et al, were determined to be 15-18% of particulate matter, with ash levels of 8-15% shown. Data was gathered from three mid 90's diesels using 480 ppm<sub>w</sub> fuel. Of the VOF, as much as 80% was found to be from lubricants[22]. Llaniguez showed a 50-75% reduction in PM using FT fuels compared to 400 ppm<sub>w</sub> Sulfur diesel fuel. Therefore in this study we should expect relative VOF levels on the order of 30-40% and relative ash levels on the order of 15-30%. In theory ash emission should also correlate to oil consumption and oil ash/sulfated ash percentage. Ash levels in raw PM are expected to be lower than those calculated directly from oil consumed due to the fact the consumed oil measurements are being made using evaporated Sulfur species which are lighter and more volatile than ash containing species. This is supported by past studies showing effective trapping of 20-60% ash expected[13, 18]. Ash losses or fluctuations during collection can also be caused by capture and release of ash along the exhaust and sample piping system. Additional studies have shown metallic components from wear materials can be significant and as high as 10% of ash emitted[9]. In some samples collected

The plot below indicates the measured raw PM emissions from tests using high Sulfur oil along with the calculated maximum ash expected, estimated by multiplying the lube oil consumption measured in section 4.3 by the sulfated ash content. Lube oil consumption of the low Sulfur oil is assumed to be the same, so with an ash level of 1% as measured in the previous section we can expect similar raw PM and ash from fuel results with low Sulfur oil producing approximately 50-66% of the ash from high Sulfur oil. Approximately half of the calculated expected ash may come from fuel. This is based on an assumption of .0005% ash in the FT fuel. FT fuel specifications list <.001% ash content. Tests using thermogravimetric apparatus here can only be assumed to be accurate to a value of <.1%. Oil consumed is assumed to be representative of the entire fluid with ash particles flowing in the exhaust system homogeneously. The 1000 RPM, 75% condition in particular indicates calculated ash levels equal to that of the raw PM. In other conditions total ash is on the order of 5-20% which is consistent with results of Sharp et al, particularly if potential reductions of fuel contribution

presented by FT fuel are accounted for. Variations in oil consumption rates and overall particulate matter measured can have a significant effect on the values calculated as well.

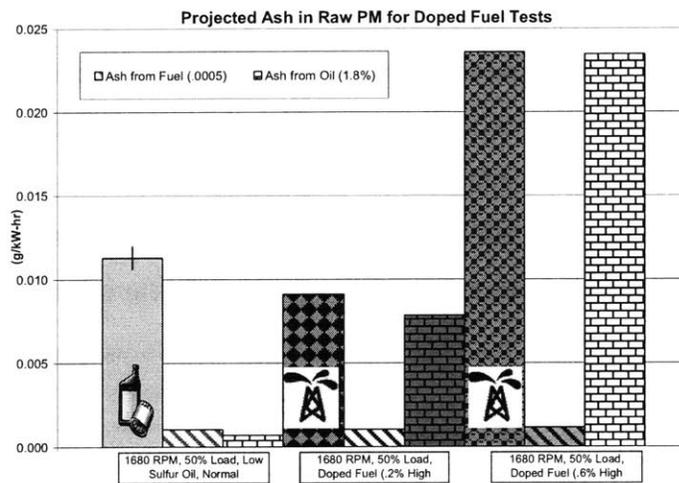
Oil ash content used for estimations of expected ash is the reported sulfated ash content which may give overestimations of potential ash. Ash levels in section 4.6 were calculated on a non-sulfated basis. These levels may be preferable for three reasons, the first being the affects of aging indicated possible dilution throughout tests. Another reason is the potential for variability in reported sulfated ash levels from manufacturers, which is generally given as an average, or typical value. The final reason is due to the use of FT fuel. With virtually no Sulfur this fuel will not be expected to sulfate the exhaust in the same manner as traditional diesel fuels. The increases in weight by sulfation are well documented and the impetus for use of sulfated ash as a parameter vice ash[39]. The difference is confirmed in section 4.6 with the lower levels of ash measured as compared to the reported Sulfated ash levels from manufacturers. Tests by Llaniguez, Acar, and Sappok at MIT all indicate significant reductions in PM levels using FT fuels as compared to low Sulfur and number two diesel. These reduced levels are believed to be linked to lower sulfate levels in the exhaust as it leaves the cylinder and condenses. Values for ash composition used for calculation were 1.8% for high Sulfur oil and 1.0% for low Sulfur oil.



**Figure 30 Projected ash in raw PM based on measured raw PM emission and calculated fuel and oil ash levels. (Included in Appendix C)**

Results for doped fuel, shown below for high Sulfur oil doping at the A50 condition, show very different results. Calculations for ash are based on a value of lubricant consumption equal to that used for the calculations above. In this case the ‘normal’ lubricant consumption

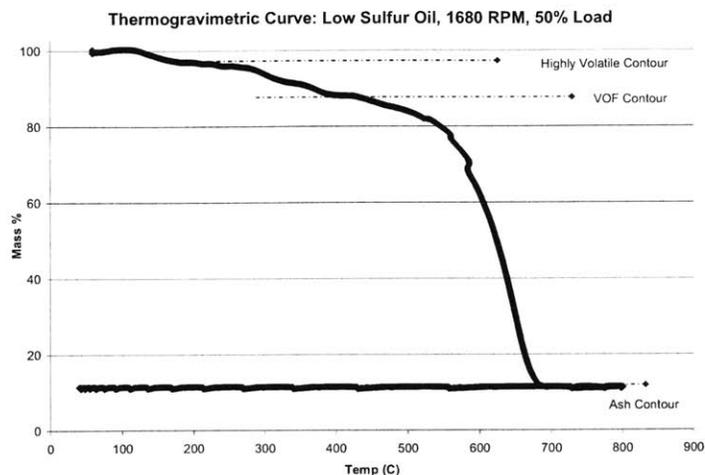
component of the ash is the low Sulfur oil in the sump and lubrication system, which is assumed to have an ash composition of 1 %. The high Sulfur oil is again assumed to have a composition of 1.8%. Based on this calculation method considerable increases in lubricant ash are assumed based on the significant increases in lubricant consumption calculated. As can be seen the ash accounts for a value greater than the amount of raw PM generated for these conditions. In addition, the lack of increase in raw PM at the .2% doping condition (center of plot) does not account for the 700% increase in ash expected. These values are likely indicative of the complications inherent in attempting to measure lubricant consumption effects by simple fuel doping, even at low levels.



**Figure 31 Projected ash in raw PM based on measured raw PM emission and calculated fuel and oil ash levels in doped fuels. (Included in Appendix C)**

#### 4.7.2 Actual Results

TGA was used to determine raw PM VOF and ash levels. A thermogravimetric curve taken from a representative sample is included below. Tests showed a distinct plateau at approximately 550-600°C, consistent with findings in other studies[44, 45, 54]. The location of the plateau at 550°C is lower than the soot detection plateau of 750°C used in ASTM D5967 for characterization of soot in oil. The difference in behavior shows the direct comparisons between fuel and oil thermogravimetric behavior and that of diesel soot cannot be made and that the presence of excessive hydrocarbons in PM may alter its thermal decomposition behavior and oxidation kinetics of soot.



**Figure 32 Thermogravimetric curve of raw PM sample from representative test condition.**

Definitive plateaus were not always evident at the 150°C and 400°C temperature points. This could be due to the use of an air atmosphere vice an inert one for the estimation of volatile organics as discussed previously for the oil and fuel tests. The 400°C point of estimation for VOF is therefore a reference. This should not adversely affect trends in data between test points and oils, however it might affect absolute values as compared to those measured by other researchers.

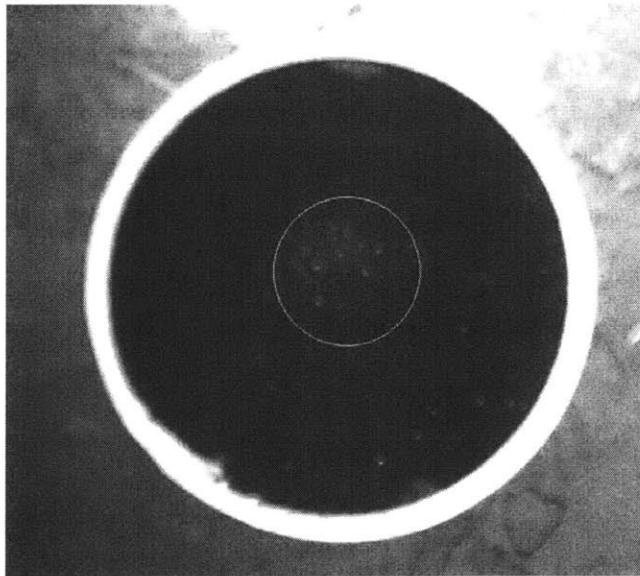
The preceding figure shows a detailed TGA curve corrected for temperature and drift effects. The following table summarizes the results obtained for each condition tested. The results are given on a dry basis, with percentage values given in terms of the percentage of raw PM calculated after high volatiles have evaporated at 150°C. This should provide a more accurate measure of ash content by eliminating any filter/sample conditioning effects due to humidity. Also, according to reports from Cummins engineers, plastic petri dishes have been known to leach volatile organic compounds into filter samples[31]. The effect of this on results obtained is expected to be small given the short duration of time between engine tests and TGA analysis. Samples were initially weighed and analyzed in a low humidity environment as discussed in earlier sections, hence values for raw PM should account for a relatively dry sample. High volatiles were generally found to be on the order of 5% or less. According to thermogravimetric results FT fuel contributed volatiles can also be expected to evaporate at 150°C. The use of a dry basis should more accurately portray the measured VOF content as a contributor of unburned lubricant contribution.

Most conditions were only tested using one sample due to amount of sample available and experimental cost. Appendix C contains a more detailed table of results including calculated uncertainties at the given test conditions. Uncertainties for raw PM were calculated as described before. Uncertainty for lubricant consumption is based on the standard deviation of recorded consumption over the period tested as described earlier. Due to high variation from what is expected to be electrical noise and the low values of oil consumption recorded at some test conditions the error can be quite high at 20%-30%. Uncertainty in TGA derived values, those being high volatiles, VOF, and ash expected are based on a  $\pm .005\text{mg}$  error observed on the TGA and the sample size, which ranged from .4-.75 mg. Hence, the predicted uncertainty for TGA analysis is  $\pm .7\%_{\text{wt}}-1.2\%_{\text{wt}}$ . Combined uncertainty, used to estimate the impact on absolute values of VOF and Ash calculated (g/kW-hr) below, ranged from  $\pm 4\%-12\%$ . Uncertainty for estimated ash expected values was also determined based on the filter and oil consumption uncertainties. Fuel and oil ash composition values were not considered as they are hard to determine. The calculation of the percentage of ash collected is helpful in determining whether or not the experimental results are correct to within an order of magnitude. They are of little other use given the last two uncertainties.

**Table 11 Summary of VOC and ash in raw PM data. (Included in Appendix C)**

Test Condition and Lubricant	Raw PM	LOC	High Vol	VOF	VOF	VOF	Ash	Ash	Ash	Est Ash (oil)	Estimated Ash (Total)	Estimated Ash Meas. (Total)
	g/kW-hr	g/hr	%wet	%dry	g/kW-hr	g/hr	%dry	g/kW-hr	g/hr	%	%	%
A50 Low Sulfur Oil	0.011	5.8	3.0	11.0	0.0012	0.099	11	0.0012	0.099	8.0	17.0	64.7
A50 High Sulfur Oil	0.011	5.8	1.5	10.0	0.0011	0.088	15	0.0016	0.128	12.0	21.0	69.0
A50 Low Sulfur Oil (fuel doped .6% High S Oil)	0.024	102.0	3.5	17.0	0.0040	0.321	43	0.0100	0.802	100.0	104.0	40.9
A50 Low Sulfur Oil (fuel doped .2% High S Oil)	0.009	36.0	4.0	13.0	0.0012	0.095	17	0.0015	0.124	87.0	98.0	17.3
A50 High Sulfur Oil (gasket material)	0.011	5.8	1.0	9.0	0.0010	0.081	16	0.0018	0.143	11.0	20.0	80.0
A50 High Sulfur fuel (.001% ash), Low S Oil	0.031	5.8	0.0	5.0	0.0015	0.124	7	0.0022	0.173	2.0	7.0	100.0
A50 High Sulfur Oil (H <sub>2</sub> SO <sub>4</sub> added)	0.011	5.8	Nd	7.0	0.0008	0.063	16	0.0018	0.143	11.0	20.0	80.0
B75 Low Sulfur Oil	0.007	7.5	0.5	12.0	0.0008	0.112	11	0.0008	0.102	9.0	23.0	47.8
B75 High Sulfur Oil	0.010	7.5	0.5	11.0	0.0010	0.141	12	0.0011	0.154	11.0	25.0	48.0
C75 High Sulfur Oil	0.008	12.5	11.0	24.0	0.0019	0.292	27	0.0022	0.328	19.0	33.0	81.8

Significant variation can be seen between the amount of ash expected (“Calc Ash (Total)”) and that collected (“Calc Ash Meas. (Total)”). The variation is consistent with the variability measured in studies in literature as discussed. The most likely sources of these inconsistencies are calculation and sampling effects. Fuel ash levels are generally measured at amounts less than the lower detection limits of test standards and reported as less than a certain value. Likewise fuel ash levels measured in this study were far lower than the minimum



**Figure 33 Contaminated PM sample. Metal debris highlighted.**

required for meaningful measurement using TGA[39, 96, 97]. In addition sampling system effects may also lead to variation in ash captured. Observation of samples contaminated with heavy gasket material indicated that the metallic particles accumulated in the center of the filter. This suggests heavier species may have different transport characteristics through piping and filter holders. If concentration of these species is higher in the center of the main exhaust pipe flow then extraction from the edge of this pipe as conducted in this study may draw raw PM samples with disproportionate levels of metallics. In addition adherence of heavier species to engine, exhaust, and sampling surfaces will also cause deviations between expected and measured results. The figure above shows a sample with particularly high metallic wear present. Several of the final samples collected during the study, at the A50 condition, were found to have metallic particles suspected of coming from gasket material in the exhaust system. These highly contaminated samples were used in the TGA analysis listed in the results as “A50 High Sulfur (gasket material).”

Finally the average oil consumed is of a lighter species given the consumption due to evaporation. This would tend to leave ash species in the cylinder while the lighter species are transported into the exhaust and measured using the SO<sub>2</sub> tracer technique. Calculation of ash in the aged samples in the sump suggest this is not the case, however decreases in ash levels of aged oil may be related to sooting and overall density changes. Given the high sensitivity to oil

ash composition shown, with increases of over 50% ash in raw PM given the 50% increase in estimated ash in oil, it is likely FT fuels provide little to no ash to the overall collected sample. The estimate amounts of ash in the table above are calculated based on a .0005% ash content in FT fuel resulting in an overall contribution of approximately 50% of the total ash from fuel. If fuel contribution to ash is assumed to be negligible and all ash is assumed to be oil derived then ash levels collected are higher than those expected. A detailed analysis of the ash product using XRD or a similar analysis technique would be beneficial in resolving the discrepancy.

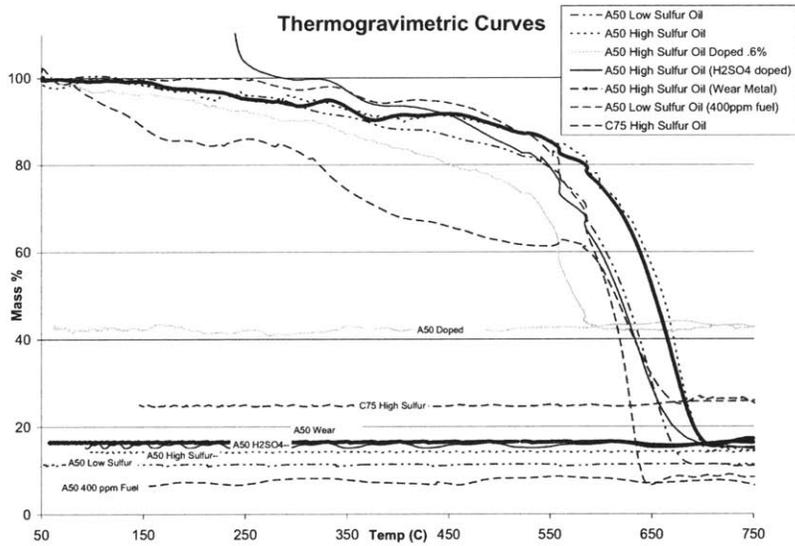
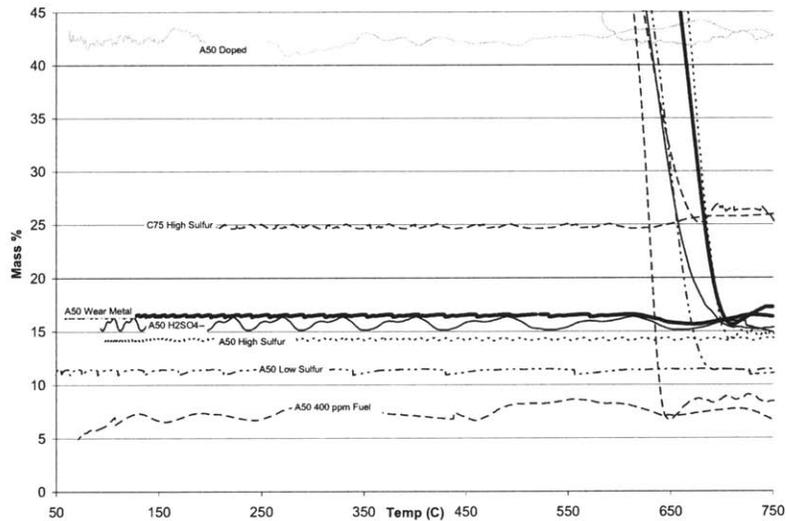
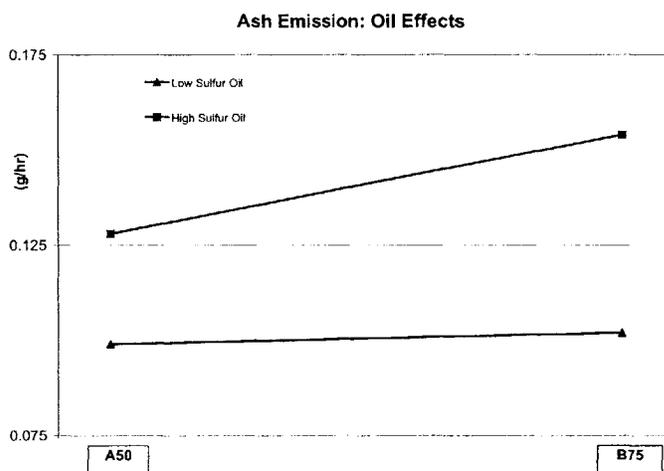


Figure 34 Thermogravimetric curves at various conditions. (Included in Appendix C)



Despite the variations in ash collected, trends were as expected. Ash emissions at given engine test conditions correlate with changes in sulfated ash levels present in the test oils. Ash levels in the raw PM from high sulfur/high sulfated ash oil tests are of a higher percentage and emission rate as those measured from the low sulfur/low sulfated ash oil. Correlation with sulfated ash levels is consistent with studies in literature. Analysis of effects of oil on ash emission are shown in the next figure. There is clearly a higher ash emission for the high Sulfur oil over the low Sulfur oil at both test conditions. Unfortunately a sufficient sample of raw PM was not available at the C75 condition with low Sulfur oil to provide a significant change in oil consumption to provide deconvolution of the fuel and oil ash effects. At these two conditions relative oil to fuel consumption is very similar, with a slightly higher oil to fuel consumption expected for the B75 condition. The plot actually indicates a slight increase in total ash emission between the two conditions as expected given the higher oil consumption at those conditions.



**Figure 35 Oil sulfated ash effects on ash emission at different engine operating conditions. (Included in Appendix C)**

VOF levels in raw PM between low and high Sulfur oils are very similar within the limits of experimental uncertainty as well at these two engine conditions. This suggests the equal oil consumption assumption for both oils is valid.

Increases in VOF and ash emission in terms of g/hr correlate to increases in engine speed and load for the A50, B75, and C75 conditions. The increase is expected given the increase in oil

consumption between the given conditions. A slight increase in VOF between conditions A50 and B75 is as expected given the slight 1.7 g/hr difference in oil consumption expected. An approximate 200% increase in VOF and ash emission correlates to the 200% increase in oil consumption between B75 and C75. The increase is near 300% between conditions A50 and C75 which is higher than expected given oil consumption estimates. This could likely be due to experimental error.

A portion of the increase in ash between high Sulfur and low Sulfur oils may be due to the effects of Sulfur on recorded ash levels. As discussed previously sulfation of exhaust metallics increases the measured ash mass. Given the zero Sulfur content of FT fuel there are significant relative increases in exhaust Sulfur levels from high Sulfur oil vs. the low Sulfur oil, therefore a potentially detectable increase in ash. The influence of Sulfur on fluid ash levels is well documented and the motivation for reporting oil sulfated ash level as opposed to just ash composition[39]. Sulfur in the form of  $H_2SO_4$  is expected to evaporate in temperatures over  $200^\circ C$ . Sulfur salts, created by the combination of metallic elements and  $H_2SO_4$  in the exhaust stream, will remain after heating. The most well known is Calcium Sulfate,  $CaSO_4$ .  $CaSO_4$  is over three times heavier than elemental Ca. Hence, the combined influences of Ca and S can significantly increase ash mass. Ca can be present in quantities as high as .4%<sub>wt</sub> in oil. In a 2.0%<sub>wt</sub> Sulfur oil sufficient Sulfur is present to react with all of the metallics present, thereby increasing the weight of ash significantly over a lower Sulfur oil. Reaction rate will also determine the amount of sulfates created. When significant Sulfur is added by fuel it is likely that sulfates will increase over that expected from oil contributed Sulfur alone. The Sulfur level therefore, whether from fuel or from high Sulfur oils used as a diagnostic technique for oil consumption measurement, can affect the resultant outcome of particulate matter and ash measured.

The formation of Zinc and Tin oxides, ZnO and SnO, also increase the relative weight of ash in comparison to a simple calculation of metallic weights, with the oxides being approximately 20% heavier than the elemental metals themselves.

With FT fuel and low Sulfur oils a significant decrease in the sulfation effect in exhaust is expected. To test this a raw PM sample collected from an FT fuel and high Sulfur oil test was saturated with significant amounts of Sulfuric acid and weighed using the TGA method used for other samples. A 1% increase in ash due to the Sulfuric acid was measured as compared to other

samples. According to the  $H_2SO_4$  supplier the residual mass left after combustion of this acid is only 2ppm, accounting for only 3 thousandths of a percent of the total raw PM sample. Several factors affect the chemical reactions of Sulfur in the cylinder and exhaust, so this method is not a true model for actual Sulfur increases from fuel or oil. It does show conclusively that increases in Sulfur levels must be considered.

Ash levels between low Sulfur (400 ppm<sub>w</sub>) and FT fuels were measured by comparing ash and VOF measurements between samples collected using the low Sulfur oil. The 400 ppm<sub>w</sub> Sulfur fuel sample was collected in a previous study by Acar[30]. An ash increase of 1.1 mg/kW-hr was detected between the two fuels, indicating higher ash levels are present in the higher Sulfur fuel samples. Despite the significant reduction in ash brought about by the change in fuels, the relative ash levels within the raw PM are much higher for FT fuel than 400ppm<sub>w</sub> fuel. This is due to the constant levels of oil derived ash between the two samples and the increased PM generated by the heavier fuel. The differences highlight the relative increase in oil affects on emissions given reductions realized from clean fuel. VOF levels between the two samples confirm similar oil consumption rates between the two tests. Overall oil effects account for less than 12% of raw PM in the high Sulfur oil sample and approximately 20% of that in the FT fuel sample. The reason for increases in ash emission using the higher Sulfur fuel are believed to be higher ash levels in the fuel itself as well as Sulfur effects described previously.

The higher percentage of highly volatile species in the C75 sample may be due to elevated Sulfuric acid condensation on the sample. Similar levels would be expected on the high Sulfur fuel sample as well. Due to significantly longer conditioning time of the high Sulfur fuel sample, a matter of months, the presence of these volatiles may have decreased due to evaporation.

## CHAPTER 5 CONCLUSION

### 5.1 Overview

Several conclusions can be drawn from the experiments conducted. These conclusions can be divided into two categories including those which were the focus of the study and those related to experimental procedure, the latter of which are included in the interest of future researchers. In general conclusions related to oil effects are drawn from the use of the two experimental commercial oils. The first contained Sulfur and ash levels typical of most common lubricants on the market. The second contained significantly higher Sulfur and ash. A Fischer Tropsch near zero Sulfur fuel was used for all tests. Conclusions regarding fuel comparisons included investigation of samples obtained using a low Sulfur (400 ppm<sub>w</sub>) fuel in a previous set of experiments conducted at MIT.

### 5.2 Engine Oil Consumption

Oil consumption in the test engine is typical for a diesel of this size and ranges from <1 g/hr at idle to approximately 36 g/hr at maximum rated speed and load. The increase is generally exponential for given loads, with oil consumption rates of less than 10 g/hr measured below 50% speed for all loads and below 50% load for all speeds. At 100% load consumption increases as much as 500% between 50% and 100% speed.

### 5.3 Effect of Oil Chemistry on SO<sub>2</sub> Emissions

Given regulatory decreases in fuel Sulfur levels to below 15 ppm<sub>w</sub> oil Sulfur level now has a significant effect on total Sulfur Dioxide and subsequent Sulfuric acid creation in and from diesel exhaust. These Sulfur levels impact the environment through direct effects as well as through increases in the level of particulate matter emitted. The high Sulfur commercial oil tested contained 4 times the Sulfur typical of most lubricants on the market and produced Sulfur Dioxide emissions equivalent to those produced by 15 ppm<sub>w</sub> fuels at high speed and load. Therefore typical engine oils can be expected to emit Sulfur Dioxide equivalent to up to 4 ppm<sub>w</sub> fuels, with higher levels in engines exhibiting greater oil consumption rates.

#### 5.4 Effect of Oil Chemistry on Raw PM Emissions

Raw PM emission rates were up to 20% higher using the high Sulfur oil as compared to low Sulfur oil over the range of conditions studied. The high Sulfur oil's higher viscosity index may lower the relative oil consumption and dampen effects of increases in raw PM emission as compared to the low Sulfur oil. TGA studies revealed similar VOF levels in raw PM gathered using both oils suggesting oil consumption rates were not vastly different, hence differences in raw PM emission are likely a result of increased ash and Sulfur levels between oils.

Assuming all VOF and ash in the collected raw PM is oil derived, lubricant contributes to approximately 25% of raw PM at mid speed and load conditions and 55% at high speed and load conditions. With FT fuels reducing raw PM emission by 50-75% the impact of oil derived effects will be proportionately lower than in tests run with typical diesel fuels.

#### 5.5 Effect of FT Fuels on the Study of Lubricant Consumption Contribution to Particulate Emissions

With raw PM emission rates up to 50% less for FT fuels over conventional diesel fuels the effect of changes in oil impact on these rates is considerably larger. For conventional fuels the differences in raw PM emission would account for less than 10% increases and likely be indistinguishable given experimental uncertainty. The lack of Sulfur in FT fuel also reduces interference and uncertainty related to fuel effects when conducting oil consumption studies using the Sulfur tracer method. Any increases in Sulfur derived particulate matter from creation of sulfates can be attributed to oil effects.

This has another consequence for the Sulfur Dioxide tracer technique. With lowered fuel Sulfur levels doping of oil for the sole purpose of oil consumption measurement can create detectable increases in ash and particulate emission which must be considered.

## 5.6 Effect of Fuel and Oil Ash Composition on Particulate and Ash Emissions

Measured ash composition can change significantly over time, with decreases in relative oil ash levels of as much as 40% measured for aged oils during the course of the study. Fuel ash levels, particularly those for FT fuel, are difficult to quantify given their extremely low concentration. Even small percentages of fuel derived ash can contribute significantly to ash in raw PM given fuel is consumed by the engine at a rate of over 10,000 times that of oil. Given the high correlation between total emitted ash and oil ash content it is likely that FT fuel contributes almost no ash to the overall particulate. Raw PM samples obtained using typical diesel fuels showed an increase in ash content over those obtained using FT fuels indicating ash levels in these fuels may be significantly higher.

## 5.7 Effect of Oil Chemistry on Ash Emission

Oil contributes significantly to the overall ash content in particulate matter, with increases correlating to oil ash and sulfated ash content. The 50-80% higher ash content measured in the higher ash oil resulted in a 50-70% measured increase in PM ash levels. This is consistent with results found in literature and indicates that FT fuel contributes extremely little to engine ash emission. Given decreases in fuel Sulfur levels, increased levels of Sulfur in oil may significantly change ash measured through the creation of sulfates of metallic species produced by engine wear and additives.

## 5.8 Effect of Fuel Chemistry on Ash Emission

Comparison of FT and 400 ppm<sub>w</sub> low Sulfur diesel obtained samples indicates significant increases in ash emissions from the latter. TGA results indicate a 200% increase in overall particulate from the higher Sulfur fuels. Sensitivity of raw PM ash to oil ash levels obtained from FT fuel derived samples suggests FT fuel contributes almost no ash to particulate. Therefore ash content in typical low Sulfur diesel fuels may contribute ash on the order of that contributed by oil. This is still considerably low considering the ratio of oil to fuel consumption is approximately 1: 10,000.

Despite the increase in ash emission the overall contribution of ash to particulate is significantly less for the higher Sulfur fuels given the increases in raw PM emission compared to FT fuels.

High fuel Sulfur levels also contribute to overall ash levels compared to samples taken using low Sulfur fuels and lubricants due to the creation of Sulfates from metallic elements present in additives.

#### 5.9 Effect of Oil and Fuel Sulfur Content and Engine Wear Metal on Emissions

Tests on raw PM samples with observably higher levels of wear debris resulted in increases in total ash collected of 10-15%. The results highlight the potentially significant impact of wear material on estimation of ash emission and the need for detailed elemental analysis of samples. Tests involving the additional saturation of raw PM samples in Sulfuric acid resulted in similar increases in estimated ash, indicating fuel and oil Sulfur effects may also contribute to higher ash emission rates, particularly as compared to those estimated using FT fuels with low Sulfur oils.

#### 5.10 Effect of Oil Doping of Fuel During Oil Consumption Tests

In addition to the obvious harmful effects of oil doping of fuels within the fuel system high level doping to accelerate oil consumption results in effects different from those seen in typical running conditions. At the mid speed and load test condition used for doping, levels of .2% resulted in lower than expected levels of ash captured for the increases in relative oil consumption as well as no discernible increases in raw PM emission. At very high levels of doping at .6% fuel the raw PM emissions increase considerably and disproportionately to that expected, with relative ash to raw PM levels significantly higher than those found in typical conditions without doping. At low speed and load conditions decreases in NO<sub>x</sub> emissions of up to 5% indicate a potential drop in cylinder temperatures for very high levels of doping.

#### 5.11 Effect of Filter Material and Weighing on Experimental Results

PTFE coated membrane filters provided significant advantages over fluorocarbon coated borosilicate glass fiber and pure quartz filters in terms of resistance to damage as well as temperature and humidity effects. For the low ambient humidity conditions experienced during this study PTFE and fluorocarbon coated filters demonstrated low uncertainty and variation to changes in conditions. Overall the greatest contributors to uncertainty in raw PM estimation were variability of the mass weighing apparatus and engine output power calculation.

### 5.12 Effect of SO<sub>2</sub> Detector Interferences on Experimental Results

Low levels of Sulfur Dioxide derived from oil consumption require particular attention when applying the Sulfur tracer technique. In particular adsorption of Sulfur Dioxide on high temperature stainless steel and steel components within the analyzer and engine were suspected of up to 30% decreases in measured emission. Correction factors derived using known oil Sulfur content combined with oil doping of fuel resulted in lube oil consumption values consistent with those expected for an engine of this size. Volatile organic fraction and ash measured in raw PM was also consistent with the oil consumption estimates.

NO was the most significant interferent in SO<sub>2</sub> measurement and required correction factors based on day to day checks using span gases. Higher than necessary O<sub>3</sub> levels generated within the test apparatus create significant errors when measuring below 1 ppm<sub>v</sub> SO<sub>2</sub>. Temperature has a significant effect on low level concentration measurement of SO<sub>2</sub> as well. O<sub>2</sub> levels in diesel exhaust allow for reductions in recommended levels of O<sub>2</sub> added during sample preparation within the Sulfur Dioxide analyzer.

### 5.13 Overall Test Procedure Effectiveness

The estimation of oil consumption by tracer method and analysis of particulate collected on small filters significantly reduces overall experimental time as compared to long term DPF collection tests. Success of the test method is highly dependent on the strict definition of ash, soot, and experimental uncertainty. The techniques used provide a rapid method for comparison of different fuels and oils in terms of their impact on aftertreatment systems.

## CHAPTER 6 RECOMMENDATIONS AND FUTURE WORK

Results reveal considerable area for future study. Uncertainty in raw PM emission rates can be reduced through increased control and monitoring of engine power output, more accurate gravimetric weighing procedures, and increased sampling. Additional TGA samples would also increase overall experimental confidence. Use of higher speed and load test points will further define oil consumption effects.

A detailed elemental analysis of test oils, fuel, particulate, and particulate ash can be conducted using advanced chemical analysis techniques. XRD, TEM, and GC/MS can characterize oil and fuel derived portions of raw PM more accurately than TGA through detailed analysis of metallic and organic composition.

Further oil consumption analysis can be conducted. In particular variation of sulfated ash in two oils with more comparable properties would reduce uncertainty related to potential differences in oil consumption rates. Likewise test matrices involving variation of metallic composition are required to further characterize the transport of particularly damaging compounds such as Sulfur and Phosphorous. These latter studies will be of greater importance as catalyst technology is applied to diesel engines.

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## APPENDICES

### Appendix A: Test Procedures and Schedules

#### A.1 Detailed engine and emission test operating procedure

	Ensure sufficient fuel/lubricant on hand 7 days prior to test
	Place filters in conditioning room 48 hours prior to tests.
	Walk around cell, ensure hose lines are attached and nothing is out of place.
	Ensure heated hose lines and gas detector exhaust lines are not touching.
	Refer to test matrix requirements, determine day's tests
	Start Electronics: <ul style="list-style-type: none"> <li>• Antek</li> <li>• No<sub>x</sub>-</li> <li>• HC- align air first</li> <li>• Computers</li> </ul>
	Start Antek ovens (1000°C) and pump heater (120°C).
	Ensure Antek backpressure valve open fully and zero air aligned to system. Open exhaust hose valve if attached for purging. Start zero air pump.
	Weigh filters required for day's tests IAW mass handling procedure. Record humidity, temperature, and pressure in addition to filter masses.
	Start Antek A/C system
	Energize heated lines <ul style="list-style-type: none"> <li>• SO<sub>2</sub> analyzer inlet piping-120°C</li> <li>• No<sub>x</sub>/HC/CO<sub>2</sub> analyzer inlet piping</li> <li>• PM sample flow piping (if raw sampling)</li> <li>• SO<sub>2</sub> analyzer heated sample hose</li> <li>• No<sub>x</sub>/HC/CO<sub>2</sub> analyzer heated sample hose</li> </ul>
	Turn key to 'on' <ul style="list-style-type: none"> <li>• Check fuel level</li> <li>• Check fuel system alignment</li> <li>• Set relative humidity meter to "no sleep"</li> <li>• Turn on fuel scale</li> </ul>
	Check oil and coolant levels
	Ensure extra oil and measuring equipment on hand if required for doping
	Put warm up filter in holder and attach to PM collection system- filters are placed rough side to mesh, smooth side to O-ring, wing nut points upstream, ensure flow meter is zeroed
	Turn on main lab "Fan" and "Pump". If other engines are running check with operators before starting.
	Ensure water aligned to engine at valve on test cell bulkhead.
	Start Labview data acquisition program VI
	Turn on "Dynamometer Power" (left button) and set initial speed required using "MANRSP" and "RPM" knob
	Ensure throttle control on engine set to 29% (idle). Note load controller on dynamometer reading to compensate in data acquisition. Typically +/- 5 RPM
	Prime fuel system by turning key on again if necessary (restart humidity meter)
	Turn on test cell fans
	Start engine <ul style="list-style-type: none"> <li>• Check for oil/water pressure</li> <li>• Run at idle for at least 10-20 minutes to warm up, some hunting can be expected.</li> </ul>
	Start Cal term (c:/ct/ct763) and load calibration files (F:/ECM)-expect alarms 195, 431, 435, 596, 951
	Check Labview settings: <ul style="list-style-type: none"> <li>• Fuel/oil properties (mass S, Aulfated Ash)</li> <li>• Expected raw PM (g/kW-hr)</li> <li>• Assumed LOC calculation method (if using S in oil calculator use this for assumed</li> </ul>

	<p>LOC, otherwise use algorithm).</p> <ul style="list-style-type: none"> <li>• Set scan/sec (reset VI)</li> <li>• SO<sub>2</sub> detector flow rate and temp</li> <li>• Filter and test condition for first run</li> <li>• Assumed NO<sub>x</sub> and HC if needed</li> <li>• Assumed fuel if needed. If not align triggers <ul style="list-style-type: none"> <li>i. “Armed” prepares to read scale when level starts changing</li> <li>ii. “Disable Trigger” disables the part of the trigger awaiting a drop. Only disable this if fuel is running in beaker.</li> <li>iii. “Use assumed” defaults back to assumed value if trigger stops calculation, otherwise maintains current kg/s calculated until trigger reengages.</li> </ul> </li> <li>• Reports: <ul style="list-style-type: none"> <li>i. “reportname.txt” for summary file</li> <li>ii. “detailed file folder/filter.condition.date” for main report</li> <li>iii. “sim files/filter.condition.date” for simulation report</li> </ul> </li> </ul>
	Bring engine to 1500 RPM, 100 NM for continued warm-up
	If sufficiently warm switch to CalTerm and disable T_Emo_Cond to set chi value back to 1 to prevent ramping
	@ 60°C oil temperature bring engine to 150 NM
	@ 80-90°C oil temperature bring engine to desired test condition
	Turn on O <sub>2</sub> gas for SO <sub>2</sub> analyzer
	Energize UV lamp and O <sub>3</sub> generator for SO <sub>2</sub> analyzer, turn on dryer gas. Auto zero analyzer
	Fill fuel beaker to level and dope with oil if needed.
	Turn PM sample pump on to purge lines
	<p>Calibrate NO<sub>x</sub> analyzer using appropriate span gas</p> <ul style="list-style-type: none"> <li>• Ensure zero gas running, “NO” selected (light off)</li> <li>• Set dial to Zero and zero analyzer, ensure constant sample pressure.</li> <li>• Set range to 4 (=1000ppm) and source valve dial to Span</li> <li>• Ensure SO<sub>2</sub> analyzer NO supply is not aligned!</li> <li>• Span with span gas at 10-20 psi to ensure same sample pressure as that zeroed</li> <li>• Switch back to zero and check</li> <li>• Switch back to sample</li> </ul>
	<p>Calibrate HC analyzer</p> <ul style="list-style-type: none"> <li>• Close NO<sub>x</sub> sample supply and open HC supply, ensure zero gas running to NO<sub>x</sub> analyzer.</li> <li>• Ensure ignited and fuel and air and zero gas supplied.</li> <li>• Set to range 1 and zero (ensure constant pressure)</li> <li>• Set to appropriate range and span (same pressure as zero)</li> <li>• Set to range 1 and check zero</li> <li>• Close HC supply and open NO<sub>x</sub> analyzer supply valve</li> </ul>
	<p>Open SO<sub>2</sub> analyzer backpressure valve, Align zero (test cell) air to analyzer and start pump.</p> <ul style="list-style-type: none"> <li>• Increase backpressure to 7psi</li> <li>• Auto zero</li> <li>• Check for stability (+/- .1 ppm)</li> <li>• Open backpressure valve</li> <li>• Switch to SO<sub>2</sub> span gas (very low pressure!) on sample box</li> <li>• Increase backpressure to 7psi</li> <li>• Span using 1s or 10s averages on Labview</li> <li>• Open backpressure valve</li> <li>• Switch back to zero air</li> <li>• Increase backpressure to 7psi and check zero</li> <li>• Open backpressure valve</li> <li>• Switch to NO span (again low pressure!)</li> </ul>

	<ul style="list-style-type: none"> <li>• Increase backpressure to 7psi and check to see zero</li> <li>• Open backpressure valve</li> <li>• Repeat NO spans for all values required.</li> <li>• Switch back to zero and check</li> </ul>
	<p>Open sample hoses and start samples to NO<sub>x</sub>, SO<sub>2</sub> analyzers</p> <ul style="list-style-type: none"> <li>• For NO<sub>x</sub>, switch to Sample, ensure in “NO” mode</li> <li>• For SO<sub>2</sub> ensure upper box temp stable</li> </ul>
	Load filter holder with sample filter, ensure number listed in Labview
	Remove warm-up filter and put filter in place
	<p>2) Double-check fuel trigger settings in Labview.</p> <ul style="list-style-type: none"> <li>• If rapid rate expected: Set “Use assumed” to no; Set trigger to “armed”; Set “disable trigger” to no</li> <li>• If slow expected: Set “use assumed to yes if value known; Set trigger to “armed”; Start fueling; Return to computer and “disable trigger” (should start calculations)</li> </ul>
	<p>Start “Write Report” (40 sec delay starts)</p> <ul style="list-style-type: none"> <li>• At 35-40 seconds open valve filter then start pump</li> </ul>
	Check to ensure report is writing
	Write simulator file if desired
	Take notes on test characteristics, anything out of the ordinary
	When fuel below trigger level switch valves to tank supply and return. Ensure proper assumed value in Labview prior to switch
	Reload spare filter holder
	Fuel engine if needed, mix next beaker of fuel if needed
	Just after end of run turn off PM pump and remove holder
	Take pressure trace, HC, and NO <sub>x</sub> measurements if desired
	TEST 1 DONE
	Bring engine to new desired test condition
	Return to check Labview settings above and run additional tests. Calibrate analyzers as necessary.
	At end of last run PREP FOR SHUTDOWN
	Decrease engine load to 100 NM
	Burn down beaker fuel
	Remove NO <sub>x</sub> /HC hose from engine and allow to flow through for purge
	Decrease SO <sub>2</sub> analyzer backpressure and remove sample hose
	Reduce Engine speed to idle
	Decrease backpressure and Switch SO <sub>2</sub> analyzer to zero gas air (keep exhaust open to allow flow through)
	Shift HC and NO <sub>x</sub> analyzers to zero
	Turn off heated sample hoses (will take some time to cool)
	After 20 minutes shut down engine with CalTerm, leave ignition on, allow more time if needed for high heat
	Escape out of CalTerm
	Turn off SO <sub>2</sub> analyzer O <sub>3</sub> generator and UV
	Secure SO <sub>2</sub> analyzer furnaces and pump and decrease backpressure
	Align zero gas pump to Antek so it can flow air through
	Secure SO <sub>2</sub> analyzer dryer, span, and O <sub>2</sub> gases
	Turn off fuel and air to HFID
	Turn off NO <sub>x</sub> analyzer
	Ensure all NO <sub>x</sub> /HC gas lines are secured-
	When below 200°C, turn off HFID
	Carry fuel and oil beakers and supplies back to their proper location
	Refuel if needed
	Secure valves and heated lines to analyzers and shut down for the night
	Turn off main lab pump and fan

	Remove filters from final holders and place in petri dishes for transport
	Take filters to conditioning room, place in completed samples box
	If cylinder 6 cooled to 50°C secure ignition
	Complete a final walkthrough of test cell prior to lockup, ensure all lines and power are secured. Secure test cell fans
	Exit out of Labview
	Place lab notes in lab folder

## A.2 Detailed mass handling procedure

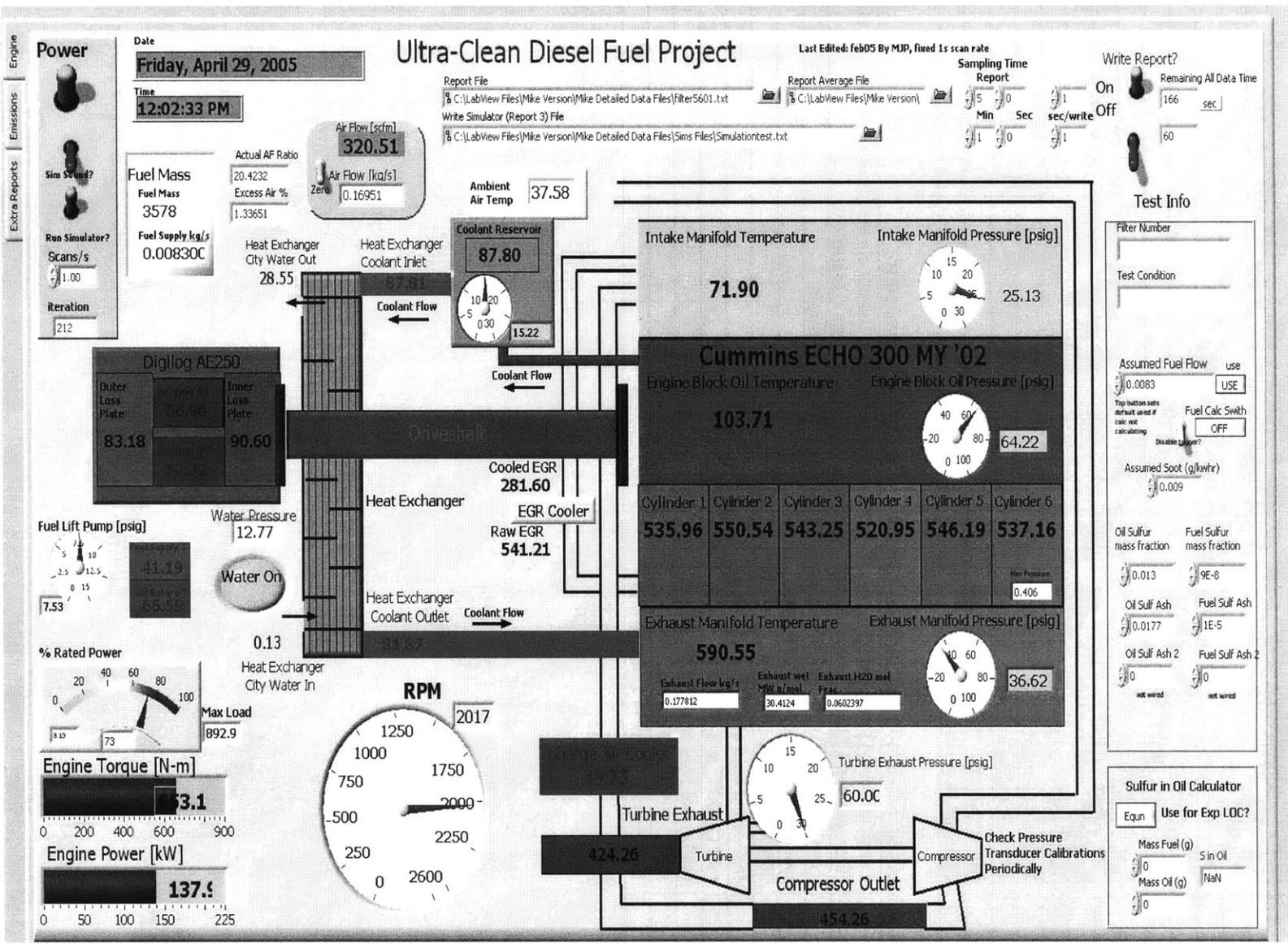
	Two 'room filters' of each material identified for tracking of ambient conditions in the weigh room IAW 40CFR86. These are referred to as control filters and are used as checks for the tare filters as well.
	Tare filter identified for each filter or filter group. The tare filters of the same material and size. Tare filters and sampling filters are identified, numbered, and conditioned for 48 hours in the conditioning room. Tare filters differ from control filters in that they travel with the sampling filters to help reduce some of the transport effects and those of changing humidity and temperature.
	Balance cycled four times using the metal calibration control weight to prevent some drift effects[26]. Metal weight can be used for checking buoyancy effects of filters.
	Ambient pressure, date, time, temperature, and relative humidity must be recorded. Use two control filters to check ambient condition effects
	Record <u>difference</u> of filter-tare. This tare method is shown to reduce balance drift effects[26]. This step was repeated three times for each filter based on past repeatability demonstrated in previous studies[30].
	Transport filters to the test environment only as needed.
	Following testing filters immediately returned to the control room for a 24 hour period.
	Scale was recalibrated and zeroed following above procedure.
	Control and tare filters weighed and compared to last measurement (this was to account for any temperature or humidity change in the conditioning room from the last weighing, in the event the control room is the same as required conditions this is not needed).
	Steps repeated for the now unloaded tare and loaded sample filters.
	Calculations of uncertainty were made and tabulated[93].

### A.3 Detailed TGA oil analysis program and handling procedure

	Zero instrument with N <sub>2</sub> purge gas and load approx 15-30mg sample (if test will run completely with air purge use zero grade air in lieu of N <sub>2</sub> )
	Isothermal hold at 30°C for 5 min (for FT fuel use 25°C for 1 minute due to higher volatility)
	30°C-200°C at 10°C/min
	200°C-600°C at 25°C/min (smaller increments may be desired)
	Isothermal hold at 600°C for 1 min
	600°C-650°C at 10°C/min
	Isothermal hold at 650°C for 5 min
	Switch to Air purge
	Isothermal hold at 650°C for 5 min
	650°C-750°C at 10°C/min
	Isothermal hold at 775°C for 20 min
	775°C-850°C at 10°C/min
	Isothermal hold at 850°C for 5 min
	Cool and read final weight

### A.4 Detailed TGA raw PM analysis program and handling procedure

	Carefully remove raw PM from top of filter using non-metallic, solvent cleaned instrument. Ensure no filter material is removed with sample. Confirm under microscope if suspected.
	Zero instrument with Air purge gas and load approx .5-1.0mg sample
	Isothermal hold at 50°C for 5 min
	50°C-800°C at 8-10°C/min
	Isothermal hold at 600°C for .2 min
	600°C-800°C at 8-10°C/min
	Isothermal hold at 800°C for 10 min
	800°C-50°C at 50°C/min
	Isothermal hold at 50°C for 30 min

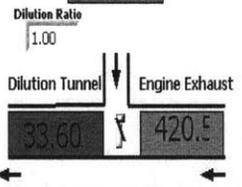


Engine  
Emissions  
Extra Reports

PM Sample Flow Rate (L/min)	PM Sample [kg/s]	PM Sample Pressure (Pa)	PM Sample % Total Exhaust (wt frac)
94.116	1.79426	101325	0.010908
Initial PM Sample Flow Rate (L/min)	PM Sample Flow % Initial (r)	Accumulated PM Sample (g)	
160	0.522867	245.319	

Relative Humidity  
9.033

Ambient Temperature  
37.58



California Analytical Instruments Model 300-HFID

HC Concentration [PPM C<sub>3</sub>H<sub>8</sub>]  
10.0

Flame On  
Range 1 Range 2 Range 3 Range 4

California Analytical Instruments Model

CO<sub>2</sub> Concentration [Vol. %]  
0.00

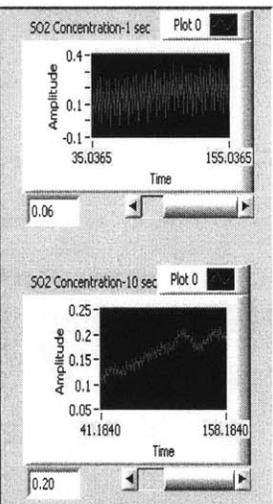
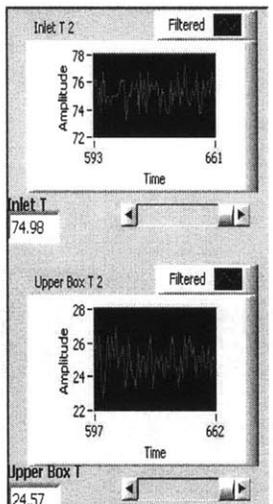
Antek Instruments Model 6000SE

SO<sub>2</sub> Concentration 1sec [ppm]  
0.06

Antek Exh Flowrate (cc/min) 14.7  
Antek Sample Flowrate (cc/min) 1.03  
Antek Samp Temp (C) 25

Antek Sample % Total exh (frac) 0.00  
Antek Sample (kg/s) 0.00

Manual SO<sub>2</sub> 285  
Temp Corr SO<sub>2</sub> 0



L/O Consumption (g/s)  
0.0026  
1.47E-5  
LOC (% exh)

L/O Consumption (g/hr)  
9.4117

LOC-g/hr - 1sec Plot 0  
Amplitude vs Time (41.4296-160.4296)  
9.41

California Analytical Instruments Model 400-HCLD

NO<sub>x</sub> Concentration [PPM]  
292.0

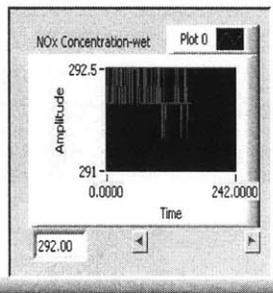
Manual 285

NO<sub>x</sub> Range 2 Range 3 Range 4 Range 5

Nox Correction for SO<sub>2</sub>?

Response [ppm SO <sub>2</sub> ]	Nox [ppm]
0.05	0
0.1	300
0.5	1000
30	3000
30	3000

Nox [PPM dry] 311  
Nox Attenuation 0.106



Engine  
 Emissions  
 Extra Reports

Run Simulator File  
 C:\LabView Files\Mike Version\Mike Detailed Data Files\Sims Files\87505Apr05wLC.txt  
 Must select simulator option BEFORE running

Report 2 File  
 Report 2 Average File  
 C:\Documents and Settings\

Remaining Report 2 Time  
 60

**Expected Results**

Expected LOC (g/s)  
 0.007246    4.07E-5  
 Expected LOC (% ash)

Expected Soot (g/s)  
 0.000345    1.94E-6  
 Expected Soot (% ash)

Fuel Sulf Ash (g/s)  
 0.000083  
 Fuel Sulf Ash (% ash)  
 0.39    0.66  
 Fuel Sulf Ash-SO2 (% ash)

Fuel Sulf Ash (% soot)  
 0.24  
 Fuel Sulf Ash (% Enh)  
 4.67E-7

Oil Sulf Ash-asmtd (g/s)  
 0.000128  
 Oil Sulf Ash (% ash)  
 0.61  
 Oil Sulf Ash (% soot)  
 0.37  
 Oil Sulf Ash (% Enh)  
 7.21E-7

Oil Sulf Ash-SO2 (g/s)  
 0.000042  
 Oil Sulf Ash-SO2 (% ash)  
 0.34  
 Oil Sulf Ash-SO2 (% soot)  
 0.12  
 Oil Sulf Ash-SO2 (% Enh)  
 2.38E-7

Total Ash (g/s)  
 0.000211  
 Total Ash (% soot)  
 0.61  
 Total Ash (% Enh)  
 1.19E-6

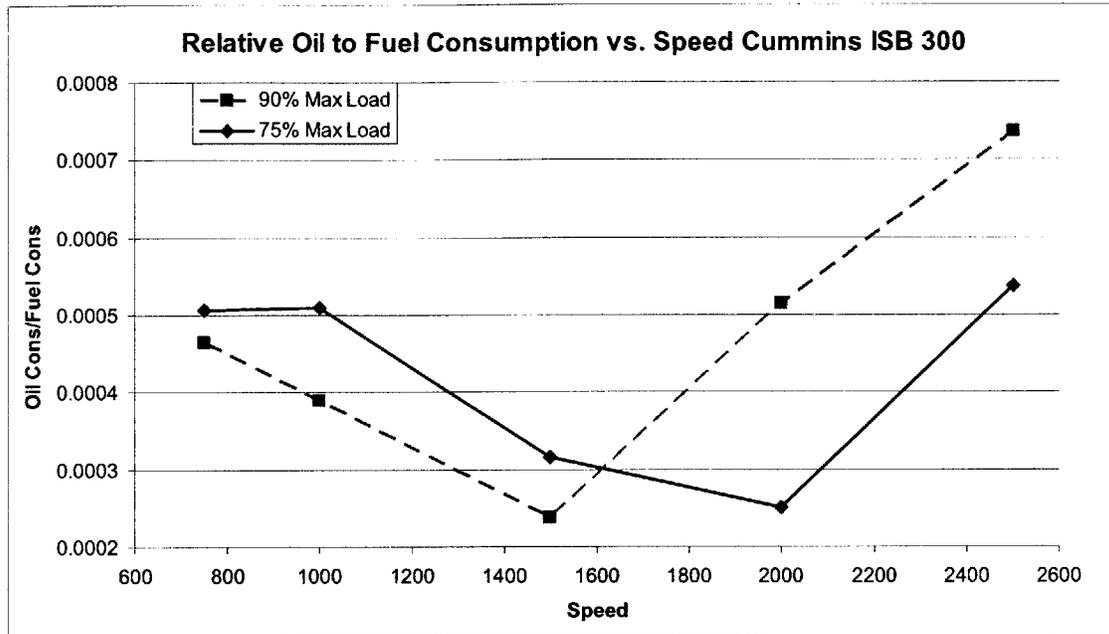
Total Ash-SO2 (g/s)  
 0.000125  
 Total Ash-SO2 (% soot)  
 0.36  
 Total Ash-SO2 (% Enh)  
 7.05E-7

**Raw Data Array**

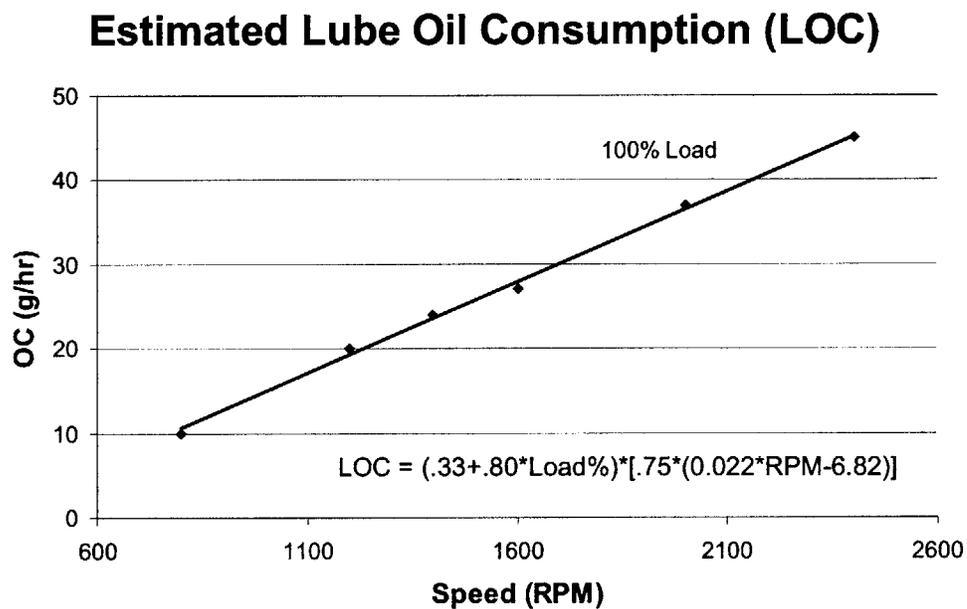
0	2016	645.5	320.8
0	0	0	0
0	0	0	0
0	0	0	0
0	0	0	0

Appendix C: Figures and Tables, Expanded View

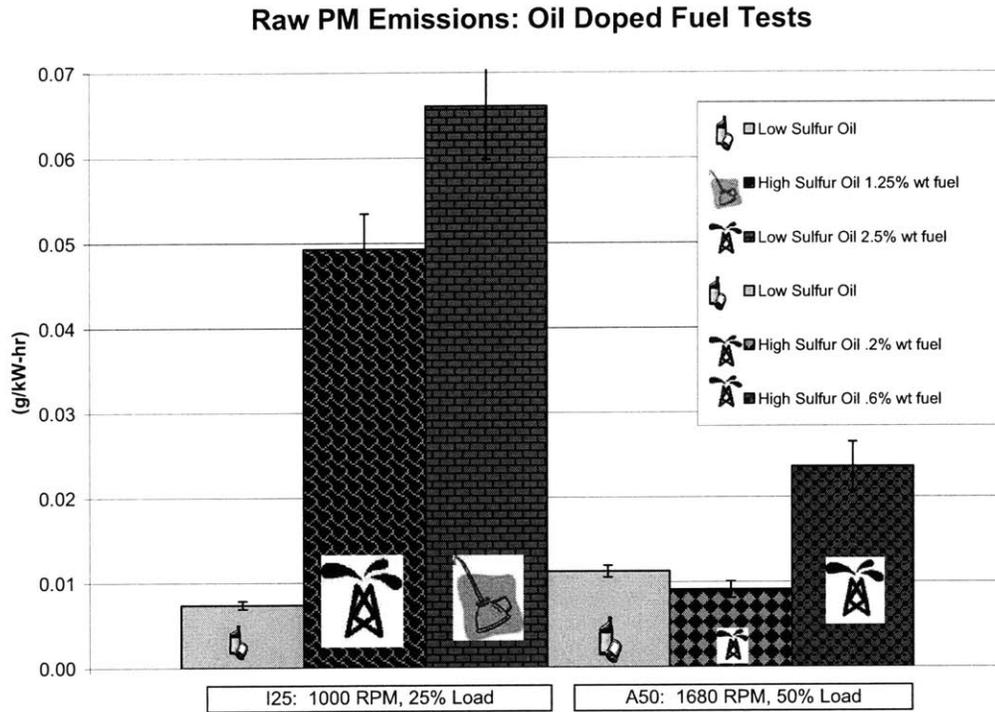
C.1 Figure 3 Relative Oil to Fuel Consumption on MY02 Cummins 6 Cylinder ISB 300 Diesel.



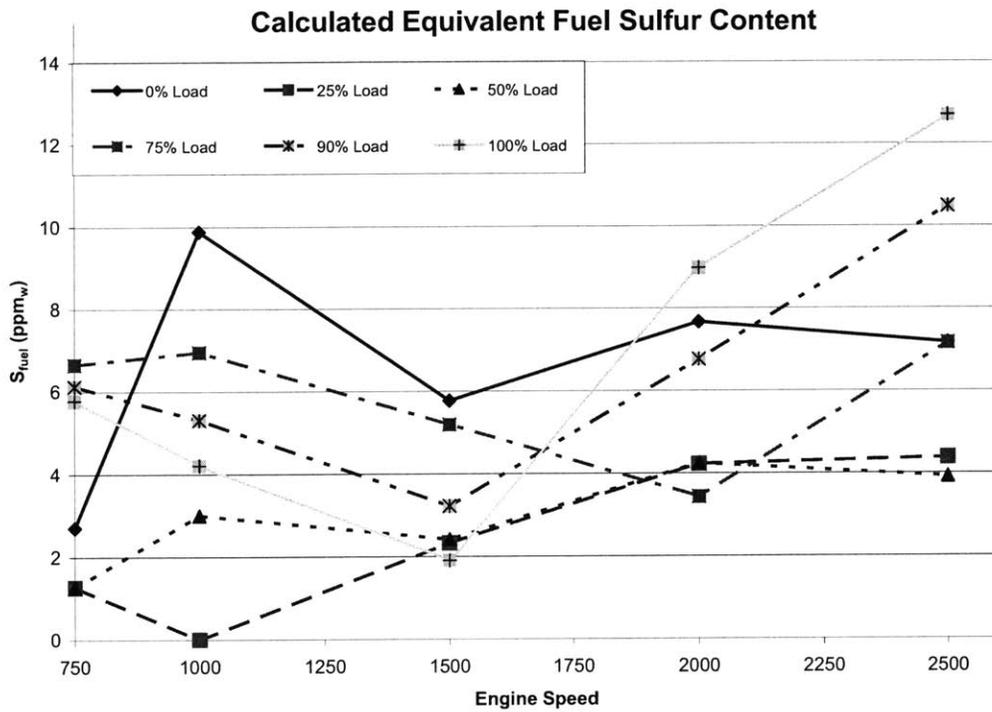
C.2 Figure 14 Estimated oil consumption model based on literature results.



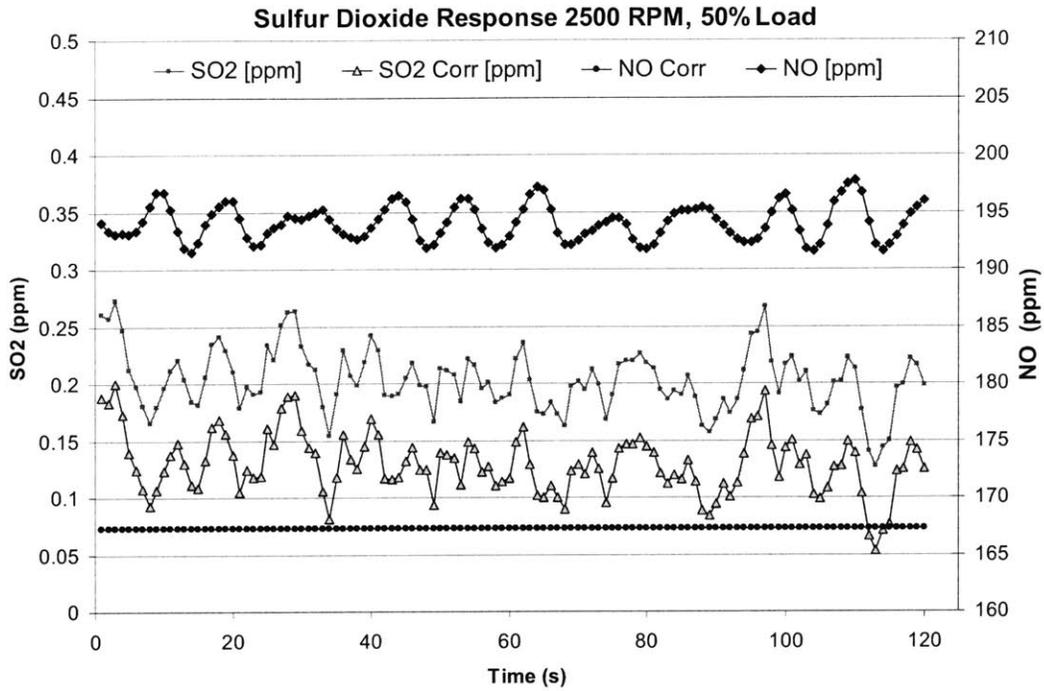
C.3 Figure 17 Raw PM emission during accelerated oil consumption tests.



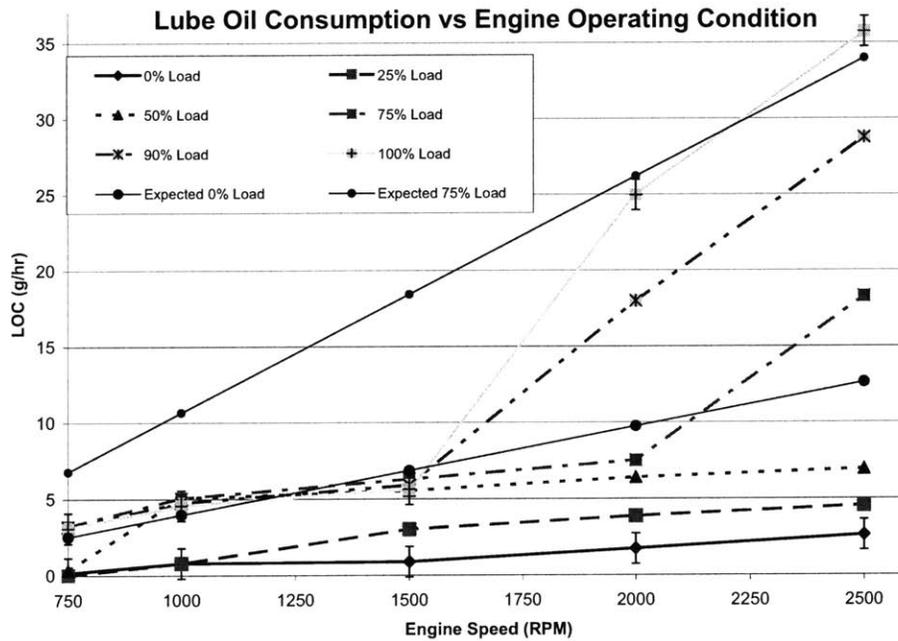
C.4 Figure 19 Calculated equivalent fuel Sulfur content.



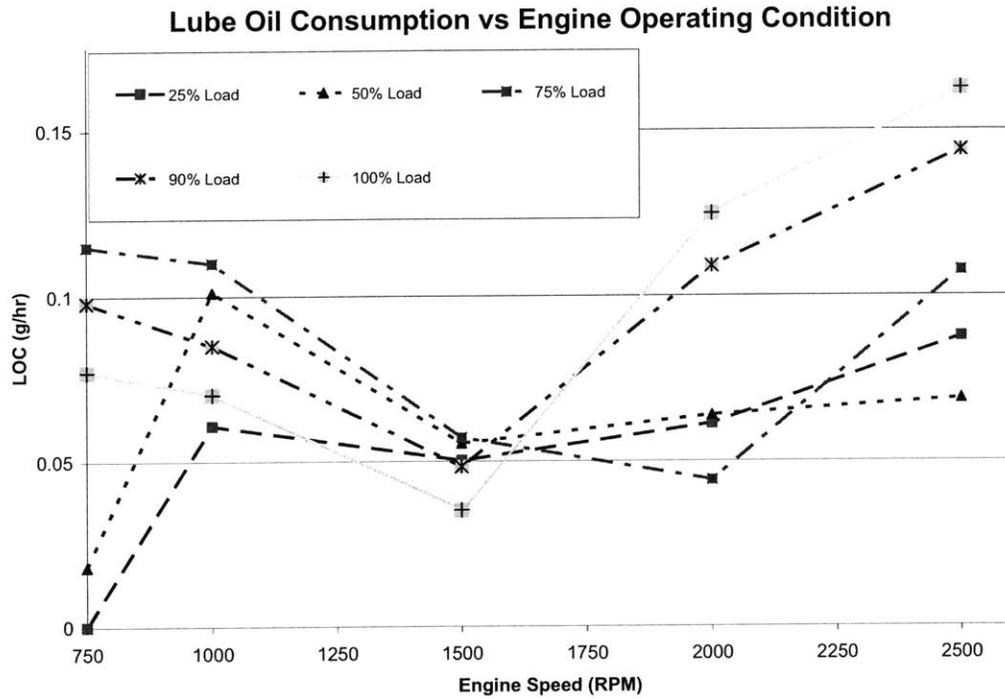
C.5 Figure 20 Sulfur Dioxide detector response and NO corrections for steady state condition.



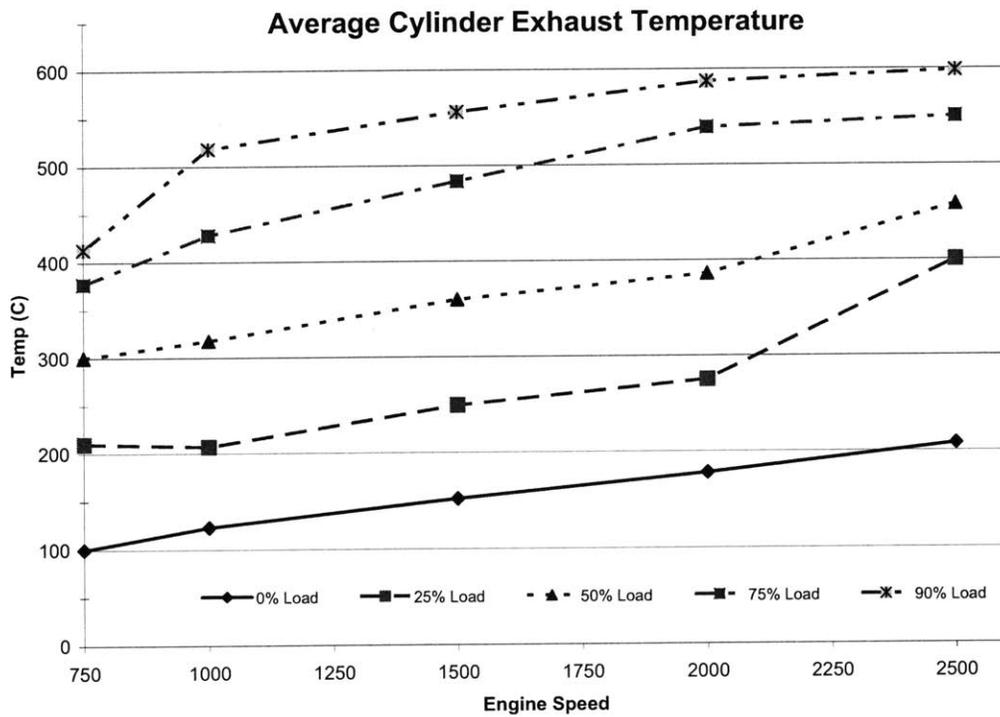
C.6 Figure 21 Measured lube oil consumption vs. engine conditions. Uncertainty levels indicated for 0% and 100% load are typical for all those measured.



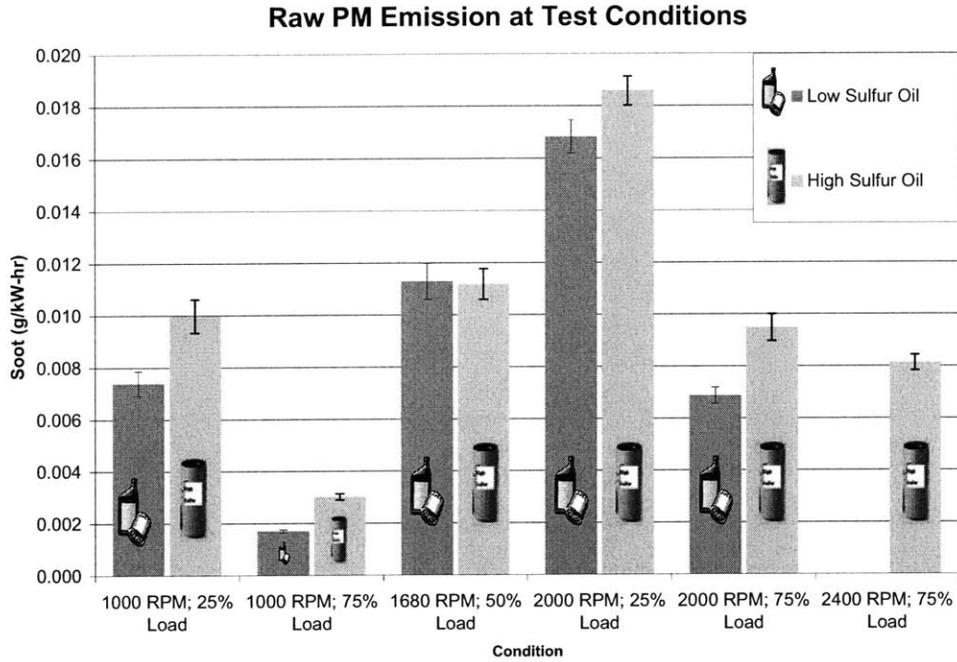
C.7 Figure 22 Measured lube oil consumption vs. engine conditions in g/kW-hr



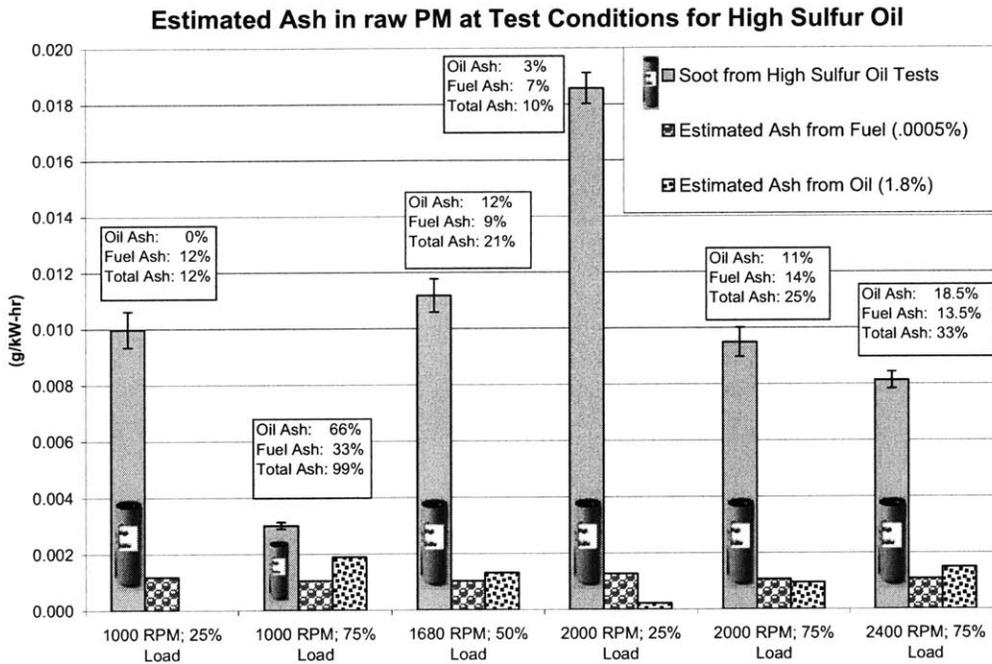
C.8 Figure 23 Average cylinder exhaust temperature variation.



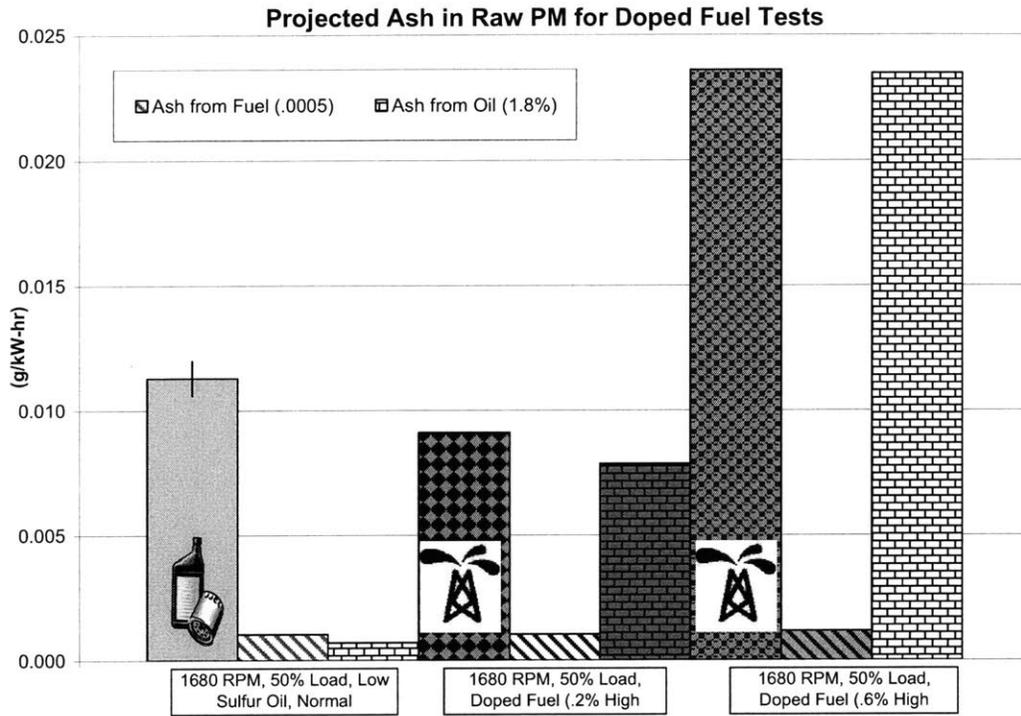
C.9 Figure 24 Raw PM emission for varying test conditions and oils



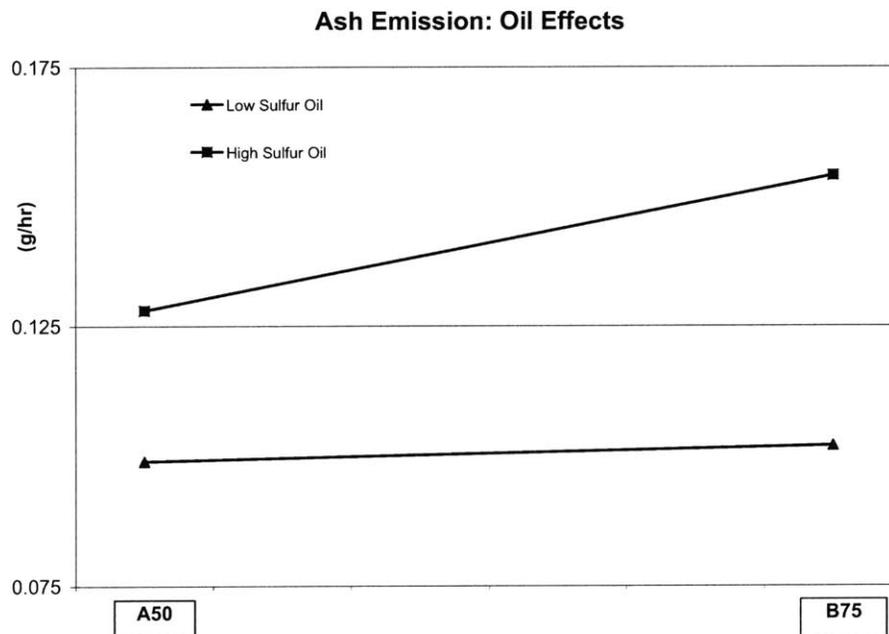
C.10 Figure 30 Projected ash in raw PM based on measured raw PM emission and calculated fuel and oil ash levels.



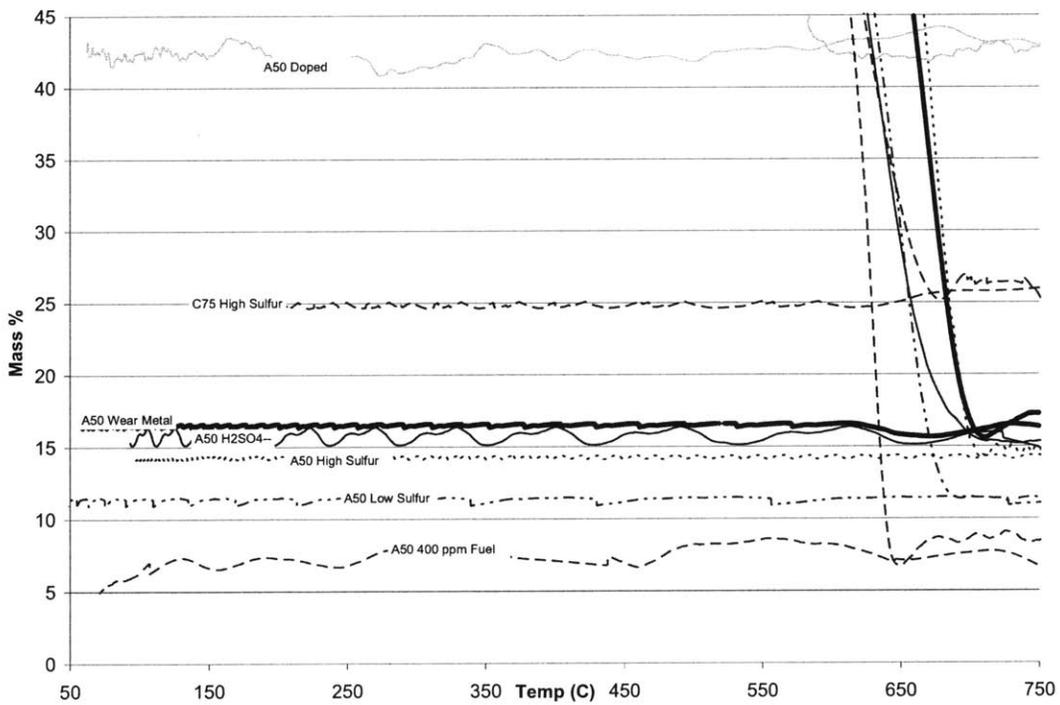
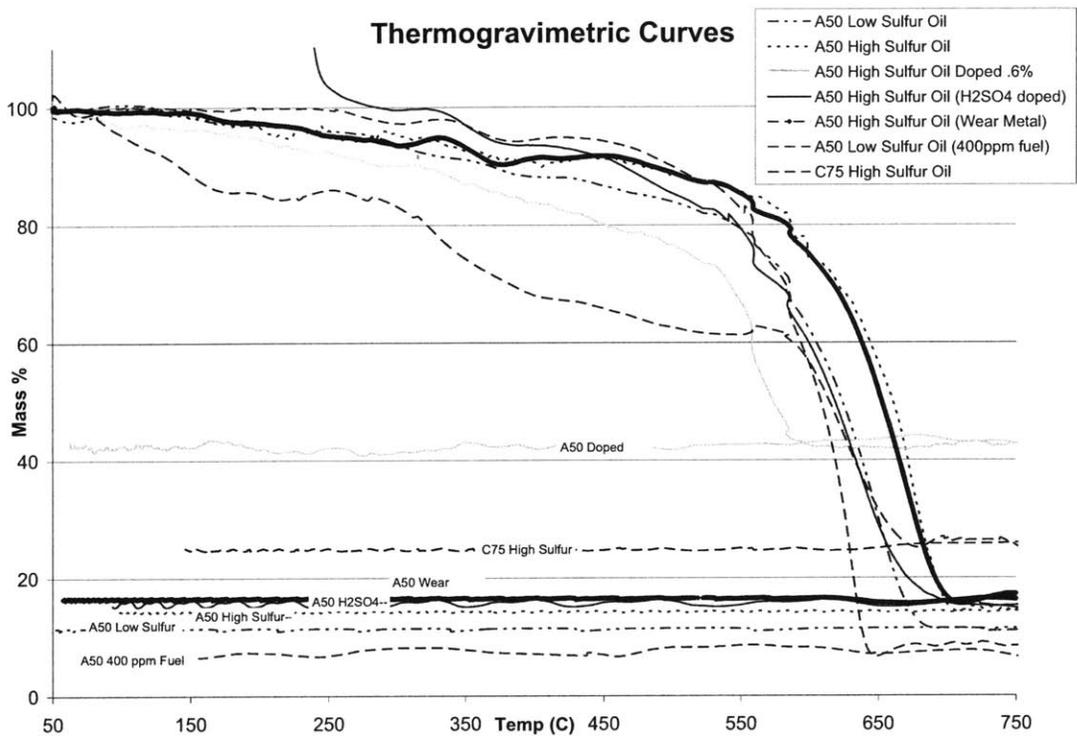
C.11 Figure 31 Projected ash in raw PM based on measured raw PM emission and calculated fuel and oil ash levels for doped fuels.



C.12 Figure 35 Oil sulfated ash effects on ash emission at different engine operating conditions.



C.13 Figure 34 Thermogravimetric curves at various conditions.



Test Condition and Lubricant	Raw PM g/kW-hr	LOC g/hr	High Vol %wet	VOF %dry	VOF g/kW-hr	VOF g/hr	Ash %dry	Ash g/kW-hr	Ash g/hr	Est Ash (oil) %	Estimated Ash (Total) %	Estimated Ash Meas. (Total) %
A50 Low Sulfur Oil	0.011	5.8	3.0	11.0	0.0012	0.099	11	0.0012	0.099	8.0	17.0	64.7
A50 High Sulfur Oil	0.011	5.8	1.5	10.0	0.0011	0.088	15	0.0016	0.128	12.0	21.0	69.0
A50 Low Sulfur Oil (fuel doped 6% High S Oil)	0.024	102.0	3.5	17.0	0.0040	0.321	43	0.0100	0.802	100.0	104.0	40.9
A50 Low Sulfur Oil (fuel doped 2% High S Oil)	0.009	36.0	4.0	13.0	0.0012	0.095	17	0.0015	0.124	87.0	98.0	17.3
A50 High Sulfur Oil (gasket material)	0.011	5.8	1.0	9.0	0.0010	0.081	16	0.0018	0.143	11.0	20.0	80.0
A50 High Sulfur fuel (.001% ash), Low S Oil	0.031	5.8	0.0	5.0	0.0015	0.124	7	0.0022	0.173	2.0	7.0	100.0
A50 High Sulfur Oil (H <sub>2</sub> SO <sub>4</sub> added)	0.011	5.8	Nd	7.0	0.0008	0.063	16	0.0018	0.143	11.0	20.0	80.0
B75 Low Sulfur Oil	0.007	7.5	0.5	12.0	0.0008	0.112	11	0.0008	0.102	9.0	23.0	47.8
B75 High Sulfur Oil	0.010	7.5	0.5	11.0	0.0010	0.141	12	0.0011	0.154	11.0	25.0	48.0
C75 High Sulfur Oil	0.008	12.5	11.0	24.0	0.0019	0.292	27	0.0022	0.328	19.0	33.0	81.8

C.14 Table 11 Summary of VOC and ash in raw PM data.

C.15 Table 11 + VOF and Ash With Uncertainty

Test Condition and Lubricant	Avg Sample Size	Raw PM Emission	Raw PM Uncertainty	Lube Oil Cons	Lube Oil Cons Uncertainty	High Volatiles	TGA Assumed Uncertainty	Combined TGA/PM Uncertainty	VOF	VOF	VOF	Ash	Ash	Ash	Ash Expected (oil)	Ash Expected (Total)	Ash Expected Uncertainty	Expected Ash Captured (Total)
	(mg)	(g/kW-hr)	(+/- %)	(g/hr)	(+/- %)	(%wet)	(+/- %)	(+/- %)	(%dry)	(g/kW-hr)	(g/hr)	(%dry)	(g/kW-hr)	(g/hr)	(%)	(%)	(+/- %)	(%)
A50 Low Sulfur	0.55	0.011	6.0	5.8	20.0	3	0.9%	6.1%	11	0.0012	0.099	11	0.0012	0.099	8	17	1.5	63%
A50 High Sulfur	0.41	0.011	5.0	5.8	20.0	1.5	1.2%	5.1%	10	0.0011	0.088	14.5	0.0016	0.128	12	21	2.5	69%
A50 High Sulfur (fuel doped 6%)	0.63	0.024	10.0	102.0	10.0	3.5	0.8%	10.0%	17	0.0040	0.321	42.5	0.0100	0.802	10	104	11	41%
A50 High Sulfur (fuel doped 2%)	0.5	0.009	12.0	36.0	10.0	4	1.0%	12.0%	13	0.0012	0.095	17	0.0015	0.124	87	98	15	17%
A50 High Sulfur (gasket material)	0.64	0.011	5.0	5.8	20.0	1	0.8%	5.1%	9	0.0010	0.081	16	0.0018	0.143	11	20		80%
A50 High Sulfur fuel (400ppm, 001% ash), Low Sulfur Oil	0.75	0.031	5.0	5.8	20.0	0	0.7%	5.0%	5	0.0015	0.124	7	0.0022	0.173	2	?		100%
A50 High Sulfur oil (H2SO4 added)	0.62	0.011	5.0	5.8	20.0	nd	0.8%	5.1%	7	0.0008	0.063	16	0.0018	0.143	11	20		80%
B75 Low Sulfur	0.75	0.007	4.5	7.5	30.0	0.5	0.7%	4.5%	12	0.0008	0.112	11	0.0008	0.102	9	23	2.5	48%
B75 High Sulfur	0.69	0.010	5.5	7.5	30.0	0.5	0.7%	5.5%	11	0.0010	0.141	12	0.0011	0.154	11	25	3	48%
C75 High Sulfur	0.45	0.008	4.0	12.5	20.0	11	1.1%	4.2%	24	0.0019	0.292	27	0.0022	0.328	19	33	3	82%

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