Final Report: Study of Marine Diesel Soot Emissions Using Oxygenated Fuel Blends

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Abstract

This project explored the effectiveness of glycerol as a fuel additive to reduce or eliminate PM emissions from diesel combustion. Soot samples were collected on transmission electron microscopy (TEM) grids from the flames of each fuel blend and analyzed via TEM and energy dispersive x-ray spectroscopy (EDS). Filter samples were collected and weighed for gravimetric emissions measurements. Solvent extractions of soot filter samples were conducted to identify PAH compounds adsorbed on the soot surface. Lastly, continuous emissions measurements of gaseous and particulate emissions were collected for each fuel blend. TEM and particulate emissions measurements provided some contradictory evidence of PM particle size distributions which merit further study with additional diagnostic techniques. PM mass emissions were found elevated for fuel blends including glycerol using mass spectroscopy and gravimetric measurement techniques. Solvent extractions of soot filter samples showed that the addition of glycerol to fuel blends generally resulted in a reduction in concentration of smaller PAH compounds and an increase in concentration of larger PAH compounds adsorbed on the soot surface. Gaseous emission measurements showed a reduction in NOx emissions with the addition of glycerol to fuel blends. CO₂ emissions increased with the addition of dodecane or glycerol, as expected, with the highest energy weighted CO₂ emissions produced by glycerol as a fuel component due to its low heating value as an oxygenated fuel. Lastly, evidence suggests that both changes in particle size and soot refractive index impact optical properties of soot formed from oxygenated fuel blends. Currently, no unifying theory is evident to explain the observations. Therefore, care should be exercised when employing soot measurements of oxygenated fuels via optical diagnostic techniques assuming a standard soot refractive index.

Introduction

The marine industry accounts for approximately 3% of total global greenhouse gas emissions, 15% of global NOx, 13% of global SO_x, and 20% of global particulate matter emissions [1,2]. Current and pending vessel emissions regulations implemented by the International Maritime Organization (IMO) require vessels worldwide to meet significantly stricter emissions requirements for critical pollutants such as sulfur oxides (SOx), nitrogen oxides (NOx), carbon monoxide (CO), and particulate matter (PM). Evidence suggests that particulate matter from shipboard marine diesel engines and other combustion sources negatively impacts world health, particularly for those living or working near these emission sources [3-5]. The reduction of PM, especially small PM species less than 2.5 microns (PM2.5) is of great importance to the scientific community. Current PM reduction strategies primarily employ exhaust particle capture and filter regeneration via thermal oxidation from combustion. This strategy is employed by modern diesel particulate filters, which are costly to maintain and reduce overall plant efficiency.

Theoretical and experimental evidence in literature suggests that adding oxygenated compounds to diesel fuel can reduce or potentially eliminate PM formation by significantly modifying the soot nucleation and growth pathways during combustion [6-8]. The experimental studies conducted to date have utilized optical diagnostic techniques for measuring soot formation and did observe reductions in soot formed from oxygenated fuel blends containing tripropylene glycol monomethyl ether, methyl decanoate, and di-butyl maleate. Glycerol is an attractive oxygenated feedstock as it is an inexpensive waste product of biodiesel production with potentially desirable combustion and fuel properties when emulsified into diesel and biodiesel fuels [9]. The Marine Engine Testing and Emissions Laboratory (METEL) at Maine Maritime Academy has demonstrated some success in achieving modest emissions reductions with glycerol fuel blends in diesel engines [10] with other efforts proving inconclusive [11]. However, the underlying mechanisms driving changes in emissions are not well understood due to the complex combustion processes undergone during diesel engine combustion.

The objective of this project was to determine the effectiveness of glycerol as a fuel additive to reduce or eliminate PM emissions from diesel combustion. Diesel combustion is primarily carried out by nonpremixed streams of fuel and air burning in a diffusion flame configuration [12]. This study used a purpose-built combustion chamber and co-flow diffusion flame burner to explore the emissions effects of oxygenated fuel blends, relevant to diesel combustion. Soot samples were collected on transmission electron microscopy (TEM) grids from the flames of each fuel blend and analyzed via TEM and energy dispersive x-ray spectroscopy (EDS). Filter samples were collected and weighed for gravimetric emissions measurements. Solvent extractions of soot filter samples were conducted to identify PAH compounds adsorbed on the soot surface. Lastly, continuous emissions measurements of gaseous and particulate emissions were collected for each fuel blend. TEM and particulate emissions measurements provided some contradictory evidence of PM particle size distributions which merit further study with additional diagnostic techniques. PM mass emissions were found elevated for fuel blends including glycerol using mass spectroscopy and gravimetric measurement techniques. Solvent extractions of soot filter samples showed that the addition of glycerol to fuel blends generally resulted in a reduction in concentration of smaller PAH compounds and an increase in concentration of larger PAH compounds adsorbed on the soot surface. Gaseous emission measurements showed a

reduction in NOx emissions with the addition of glycerol to fuel blends. CO₂ emissions increased with the addition of dodecane or glycerol, as expected, with the highest energy weighted CO₂ emissions produced by glycerol as a fuel component due to its low heating value as an oxygenated fuel. Lastly, evidence suggests that both changes in particle size and soot refractive index impact optical properties of soot formed from oxygenated fuel blends. Currently, no unifying theory is evident to explain the observations. Therefore, care should be exercised when employing soot measurements of oxygenated fuels via optical diagnostic techniques assuming a standard soot refractive index.



Experimental Description

Figure 1: Combustion chamber and diffusion flame burner assembly with associated liquid and gaseous flow controllers and plumbing.

The experimental apparatus built for this study is shown in Figure 1. The assembly consists of a combustion chamber, diffusion flame burner, mass flow controllers, and plumbing. The combustion chamber consists of a 200mm cube of 4140 steel hollowed out to form a cylindrical interior volume with conical top and bottom. The top and bottom corners of the chamber were additionally chamfered to accept ports for exhaust and chamber purge. Four ports were machined into the sides for optical access with two additional ports machined into the top and bottom with the provision to accept a variety of flanged burner assemblies. Flanged extension ports were constructed to receive 2in SAE J514 sapphire windows (Rayotek Scientific, Inc.) and permit plumbing for window purge with nitrogen. All flanges were fastened with 8 bolts (SAE Grade 8 7/16"-20 UNF). Figure 2 provides additional detail of the combustion chamber.



Figure 2: Detailed drawing of combustion chamber with key dimensions provided in mm.

Figure 3 illustrates the co-flow diffusion flame burner constructed for this study. The burner consists of an inner fuel nozzle (3mm ID, 5mm OD) and outer co-annular air nozzle (1in OD). The inner fuel nozzle extends 5mm above the burner surface and is chamfered to a knife edge to minimize vortices during fuel/air mixing. The inner fuel nozzle is packed with stainless steel wool to ensure a uniform velocity profile at the nozzle exit. Similarly, the outer air nozzle is press fit with two 40 micron, 1in diameter, 1/4in thick sintered metal disks (Capstan, Inc.), again ensuring uniform air velocity at the nozzle exit. To accommodate vaporized liquid fuel testing, the burner is wrapped with fiberglass heat tracing then insulated with braided fiberglass tape.



Figure 3: Detailed drawing of burner assembly with key dimensions provided in mm.

All plumbing was made of 316L stainless steel instrumentation grade compression fittings and tubing. Plumbing associated with the liquid fuel vaporizer is illustrated in Figure 4. Beginning at the far left, gaseous fuel is introduced into a heat exchanger and preheated to aid in liquid fuel vaporization. The heat exchanger is composed of a 1/4-inch bulkhead union press fit full of 1/4inch diameter, 1/8-inch thick, 100-micron sintered 316L stainless steel disks (Capstan, Inc.). The gaseous fuel flow further acts as a carrier gas to maintain consistent fuel flow to the burner. Next, liquid fuels are introduced into the liquid fuel vaporizer, with the length and inner diameter of the liquid fuel tubing minimized (1/8-inch OD, 0.027-inch ID) to reduce deadtime in fuel blending response due to low liquid flow rates. The vaporizer is composed of a 1/8-inch union cross, 1/4 inch to 1/8-inch reducer, 1/4-inch bulkhead union, and 1/4-inch tee (for temperature monitoring via thermocouple) all packed with stainless steel wool to maximize surface area and heat transfer, ensuring complete liquid fuel vaporization. Next, a mixing chamber composed of a 10-inch length of 1-inch diameter tubing packed with stainless steel wool is used to ensure a homogenous and steady flow of fuel. Lastly, a filter composed of a 1/4-inch bulkhead union press fit full of 100-micron sintered 316L stainless steel disks is used as a flame arrester and passive pressure regulator before the vaporized fuel mixture enters the burner. All fuel plumbing is wrapped with fiberglass heat tracing then insulated with braided fiberglass tape.



Figure 4: Plumbing for liquid fuel vaporizer.

Methane (Airgas, CP Grade), dodecane (Oakwood Products, 99% purity), and glycerol (Carolina Biological, Reagent Grade) were selected in this study for fuel blending. Methane is recognized as a fuel with low soot emissions relative to other hydrocarbons and served as a carrier gas for all liquid fuel blends. Dodecane was selected as a diesel fuel surrogate while glycerol was used for its high molecular oxygen content (52% by mass). From the three pure fuels, four fuel blends were investigated for changes in soot emissions; methane, 0.9 methane + 0.1 dodecane, 0.7 methane + 0.3 glycerol, and 0.65 methane + 0.1 dodecane + 0.25 glycerol by volume. All fuel blends were vaporized and thoroughly mixed in the gaseous phase, ensuring homogenous combustion.

Gaseous flow rates of methane, air, and nitrogen were maintained by thermal mass flow controllers (Brooks SLA5850) while liquid flow rates of dodecane and glycerol were maintained by Coriolis flow controllers with liquid fuel tanks pressurized to ensure sufficient liquid fuel flow. A Bronkhorst M12 flow controller was used to regulate dodecane flow while a Bronkhorst M12 flow meter integrated with a Badger Type 807 Research Control Valve was used for glycerol. Heat tracing was further applied to all glycerol plumbing from the storage tank to the

vaporizer. The heat tracing was set to 150°F and served to reduce glycerol viscosity for effective flow control. Table 1 describes the flow rates used for each fuel blend.

Fuel Blend	Methane	Air	Nitrogen	Dodecane	Glycerol
Methane	3.132	140	550	0	0
Methane/dodecane	1.324	120	550	1.562	0
Methane/glycerol	1.608	140	550	0	3.957
Methane/dodecane/glycerol	0.957	140	550	1.563	2.1127

Table 1: Mass flow rates (in g/hr) used for each fuel blend in this study.

For methane and methane/dodecane flames, the burner, vaporizer, and high temperature heat tracing were maintained at 500°F. For methane/glycerol and methane/dodecane/glycerol flames, the burner and heat tracing were set to 560°F while the vaporizer was maintained at 570°F.

It is widely recognized that global and local mixture stoichiometry has an effect on resulting combustion emissions. Moreover, the equivalence ratio (the most often used benchmark for mixture stoichiometry) is an incomplete indicator of stoichiometry for oxygenated fuels. The oxygen ratio was introduced by Muller et al. in 2003 as a more universal measure of mixture stoichiometry [13], and is used in this study to compare fuel blends with and without oxygenated components. For this work, all fuel blends were tested at a fixed global oxygen ratio of 2.6.

Transmission Electron Microscope Analysis

Soot samples were collected on transmission electron microscope (TEM) grids (Electron Microscopy Sciences, CF200F2-Cu) in-situ from flames using a solenoid actuated sampling device. The sampling device is shown in Figure 5 and consists of a linear solenoid actuated via a relay with actuation timing controlled by LabVIEW. For each fuel blend tested, the sampling device was installed into a threaded port on the combustion chamber. Soot samples were collected at a height of 10mm +/- 0.5mm above the burner surface (HAB) and were exposed to the flame for 100ms +/- 5ms, both determined by slow motion videography. Flame exposure time is in line with previous studies [14]. Visible flame heights were determined to be 16.6mm for methane, 21.6mm for methane/dodecane, 14.3mm for methane/glycerol, and 14mm for methane/dodecane/glycerol fuel blends.



Figure 5: Solenoid actuated sampling device used for thermophoretic soot sampling of flames on TEM grids.

Soot samples collected were imaged using a Thermo Fisher Scientific Themis Z 3.1 electron microscope. Digital TEM images were analyzed using ImageJ photo processing software and the Analyze Particles function to determine aggregate area and minimum and maximum aggregate Feret diameter. Primary particle area and average diameter was also determined by fitting ellipses to primary particle outlines. Energy dispersive x-Ray spectroscopy (EDS) was further applied to the soot samples to determine elemental composition.

Analysis of Soot Filter Samples

Soot samples were collected from the exhaust port of the combustion chamber on glass fiber filters (Millipore APFF02500). A small diaphragm pump was used downstream of the filter to maintain sample flow with flow rate monitored via a flow meter (Omega Engineering Inc. FMA-A2111). Upstream piping was composed of 316L stainless steel tubing with length minimized to reduce sample losses. The filter samples were collected for approximately four hours for each fuel blend. Before and after soot sampling, each filter was dried in an oven at 200°C for 20 minutes, then massed via analytical balance (Sartorious ENTRIS224-1S). Total soot mass and sample flow volume were recorded to determine gravimetric soot emissions.

A solvent extraction procedure was conducted on the filter samples to gain insight into polycyclic aromatic hydrocarbon (PAH) compounds adsorbed on the soot surface. The solvent consisted of a 50/50 mixture of hexane and acetone by volume. Ten nanograms of internal standard consisting of four deuterated PAHs (Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, and Perylene-d12) was introduced at the start of each extraction. Each filter sample was extracted in 15 mL of solvent via ultra-sonication for 20 minutes at room temperature. Each extract was then centrifuged at 3500RPM for 20 minutes and the supernatant was decanted from the solids. This process was repeated three times, with extracts from each filter combined into one sample. Extracts were then concentrated to 0.1 mL using a rotary evaporator. The samples were analyzed via an Agilent 7000D Triple Quadrupole Gas Chromatograph/Mass Spectrometer (GCMS) equipped with a 30m, 0.25µm film HP-5MS, 0.25 mm ID capillary column in both triple quadrupole dMRM and single quadrupole scan modes. The extraction procedure was verified by applying the procedure to NIST Standard Reference Material (SRM) 2795 (Diesel Particulate Matter). The resulting concentrations of PAH compounds extracted were compared to the SRM and found in reasonable agreement.

Emissions Measurements

Particulate matter and gaseous emissions were continuously monitored from the exhaust port of the combustion chamber. An MKS 2030 hot-cell Fourier-transform infrared spectrometer (FTIR) was used to measure gaseous emissions of nitrogen oxides (NOx), CO2, CO, and total unburned hydrocarbons (THC). Acrolein, a toxic partial oxidation product of glycerol, was also monitored. The FTIR utilizes a liquid nitrogen cooled MCT detector and was operated at 0.5cm⁻¹ spectral resolution and a sampling rate of 6 samples per minute. Particulate matter emissions were monitored with a BMI model 1712 mixing condensation particle counter (MCPC) and model 2100 scanning electrical mobility spectrometer (SEMS). The MCPC features a time response of 180ms to step changes in particle concentration. The SEMS measures particles in the range of 0.01-0.5 microns and was operated at a sampling rate of 6 samples per minute.

Results

Figure 6 shows soot particulate matter collected on glass fiber filters for four fuel blends of a) methane, b) 0.9 methane + 0.1 dodecane, c) 0.7 methane + 0.3 glycerol, and d) 0.65 methane + 0.1 dodecane + 0.25 glycerol by volume. All filter samples were collected over a period of approximately four hours at steady state combustion conditions. Filter samples of methane and methane/glycerol exhibited little visual differences. The methane/dodecane filter sample exhibited black soot material, typical of diesel combustion. Notably, filter samples b) and d) of Figure 6 contain equal volume fractions of dodecane while the addition of glycerol reduced visible black soot loading to zero. These observations initiated a variety of tests to further explain the observed changes in soot loading.



Figure 6: Soot collected on glass fiber filters from four fuel blends of a) methane, b) 0.9 methane + 0.1 dodecane, c) 0.7 methane + 0.3 glycerol, and d) 0.65 methane + 0.1 dodecane + 0.25 glycerol by volume.

Transmission Electron Microscope Analysis

Figure 7 shows TEM images of soot particles collected from the flames of the four fuel blends at a height of 10mm above the burner surface (HAB). Figure 7 a) presents several average sized soot particles from a flame of pure methane. The particles are small (approximately 20nm in average geometric diameter) and composed of a small number of aggregated primary particle spherules approximately 5nm in diameter. Poor contrast is observed against the carbon film of the TEM grids due to their size. These particles are typical in size to nascent soot with insufficient reaction and flame residence time to grow, collide, and form larger mature aggregates. In contrast, Figure 7 b) shows an image of soot particles from the methane/dodecane fuel blend. These larger aggregates (approximately 100nm in average geometric diameter) are illustrative of typical soot formed from diesel combustion. The particles are composed of many primary particle spherules approximately 20nm in diameter, formed into random branched-chain structures. Image contrast against the carbon film background is improved due to the increased size and optical thickness of the particles. Figure 7 d) shows soot particles collected from the methane/dodecane/glycerol fuel blend. No reduction in average soot particle size is evident in comparison to methane/dodecane soot at 10mm HAB. Lastly, Figure 7 c) presents soot particles collected from the methane/glycerol fuel blend with average particle size observed to be similar to pure methane combustion. Note the high contrast spheres in the Fig. 7 b), c), and d) are copper nanoparticles identified by Energy Dispersive X-Ray Spectroscopy (EDS). These copper nanoparticles are observed in all samples and are a product of the copper grids used for

sampling. It has been shown that copper TEM grids coated with carbon films are unstable at high temperatures and form copper nanoparticles due to copper sublimation and diffusion between the copper grid and carbon film [15]. The effect does not impact the results of this study but does complicate the analysis procedure of TEM images.



Figure 7: TEM images of soot particles from four fuel blends of a) methane, b) 0.9 methane + 0.1 dodecane, c) 0.7 methane + 0.3 glycerol, and d) 0.65 methane + 0.1 dodecane + 0.25 glycerol by volume. Samples were collected at a height of 10mm above the burner surface.

Higher resolution TEM images reveal further detailed structural changes to the soot particles formed from different fuel blends. Methane and methane/glycerol fuels exhibited soot particles with a more amorphous carbon structure with less observable ordered layering of material. In contrast, a significant proportion of the soot formed from the methane/dodecane and methane/dodecane/glycerol fuel blends exhibited primary particles with a more ordered fine structure of layered graphitic material. Further analysis of the TEM samples by Energy

Dispersive X-Ray Spectroscopy (EDS) showed that soot material was composed of carbon with less than 1% of oxygen for all fuel blends. No change in oxygen composition was observable with changes in fuel oxygenation.

Soot particle size statistics are shown in Figures 8 and 9 from a sample of TEM images analyzed for each fuel blend. Figure 8 presents the normalized distribution of mean soot aggregate diameter calculated from the average of the minimum and maximum Feret diameter of each particle. The distributions indicate little observable change in aggregate size at 10mm above the burner surface for fuel blends of methane and methane/glycerol. The average aggregate size for the two fuel blends was 18nm +/- 2nm. The methane/dodecane and methane/dodecane/glycerol fuel blends exhibited a significantly wider aggregate size distribution with an average aggregate size of 81nm +/- 1nm. Figure 9 presents the normalized distribution of mean primary particle diameter determined by fitting elliptical areas to primary particle outlines and calculating the resulting diameter of a circle of equal area. Primary particle size distribution is shown effectively unchanged for fuel blends of methane and methane/glycerol. Both fuels exhibit average primary particle diameters of 8nm +/- 1nm. In contrast, the primary particle diameter distribution of the methane/dodecane and methane/dodecane/glycerol fuel blends is wider and shifted to larger particle size with an average primary particle diameter of 17.5nm +/- 1.5nm. Aggregate and primary particle sizes from the methane/dodecane fuel are in line with previous studies for diesel-like soot [16]. In summary, at 10mm HAB the addition of a significant proportional of glycerol to a methane/dodecane flame does not reduce soot particle aggregate and primary particle sizes significantly. Furthermore, the addition of glycerol to a methane flame does not reduce soot particle size below that of pure methane combustion.



Figure 8: Normalized distribution of mean soot aggregate diameter from four fuel blends of methane, 0.9 methane + 0.1 dodecane, 0.7 methane + 0.3 glycerol, and 0.65 methane + 0.1 dodecane + 0.25 glycerol by volume. Mean aggregate diameter is calculated from the average of the minimum and maximum Feret diameter of each particle.



Figure 9: Normalized distribution of mean soot primary particle diameter from four fuel blends of methane, 0.9 methane + 0.1 dodecane, 0.7 methane + 0.3 glycerol, and 0.65 methane + 0.1 dodecane + 0.25 glycerol by volume. Mean primary particle diameter is determined by fitting elliptical areas to primary particle outlines and calculating the resulting diameter of a circle of equal area.

GCMS Analysis of Solvent Extractions

Figure 10 shows polycyclic aromatic hydrocarbon (PAH) concentrations (in micrograms per gram of soot sample) from solvent extraction of soot filter samples for the four fuel blends of this study. All filter samples were collected over a period of approximately four hours at steady state combustion conditions. Fifteen EPA recognized priority PAH's are reported spanning sizes from two to seven benzene rings (from left to right of Fig. 10). Reported error bars show standard calibration error (the dominant error source) estimated from propagation of error of quadratic regression coefficients. The average standard deviation for repeatability was determined to be approximately 6% based on five repetitions of blank samples. The methane/dodecane fuel blend exhibits the highest PAH concentrations for compounds composed of two to four aromatic rings with an observable reduction in PAH concentrations for larger compounds of four to seven aromatic rings. In contrast, pure methane only exhibits significant PAH concentrations for two of the largest PAH compounds; Indeno[1,2,3-c,d]pyrene and Dibenz[g,h,i]perylene. The addition of glycerol in the methane/dodecane/glycerol fuel blend results in a reduction in concentration of smaller PAH compounds in the range of two to four aromatic rings and a subsequent increase in concentration of larger PAH compounds. The addition of glycerol to pure methane also shows an increase in PAH concentrations of larger compounds. Total extractable measured PAH concentration was 10.3ug/g +/- 0.8ug/g for pure methane, 1215ug/g +/- 78ug/g for methane/dodecane, 44.6ug/g +/- 4.6ug/g for methane/glycerol, and 312ug/g +/- 19ug/g for methane/dodecane/glycerol fuel blends.



Figure 10: Polycyclic aromatic hydrocarbon (PAH) concentrations from solvent extraction of soot filter samples for four fuel blends of methane, 0.9 methane + 0.1 dodecane, 0.7 methane + 0.3 glycerol, and 0.65 methane + 0.1 dodecane + 0.25 glycerol by volume.

An analysis of internal standard recovery provides further insight into the effect of fuel blend on compounds adsorbed on the soot surface. Four deuterated PAH compounds were used as internal standards in this study ranging in size from two to four aromatic rings (Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, and Perylene-d12). Figure 11 presents the recovery of these internal standard compounds from solvent extraction of soot filter samples for the four fuel blends with a blank filter used for baseline reference. A significant reduction in internal standard recovery is exhibited for the methane/dodecane fuel blend for Chrysene-d12 and Perylene-d12 internal standard compounds. The same effect was observed from testing of diesel particulate matter standard reference material. Assuming PAH compounds behave proportionally to similar sized internal standard compounds, the results suggest methane/dodecane soot exhibits strong bonding and adsorption between the soot surface and PAH compounds composed of at least four aromatic rings. In contrast, soot samples from methane, methane/glycerol, and methane/dodecane/glycerol fuels do not exhibit significant changes in internal standard recovery with respect to compound size. This indicates weaker bonding and adsorption between the soot surface and PAH compounds composed of at least four aromatic rings. Future work should investigate any potential relationship between soot particle size and/or fine structure and PAH adsorption.



Figure 11: Recovery of internal standard compounds from solvent extraction of soot filter samples for four fuel blends of methane, 0.9 methane + 0.1 dodecane, 0.7 methane + 0.3 glycerol, 0.65 methane + 0.1 dodecane + 0.25 glycerol by volume. Internal standard recovery for a blank filter is also shown for baseline reference.

Several oxygenated polycyclic aromatic hydrocarbon (Oxy-PAH) compounds were also identified and investigated for any effect from glycerol fuel oxygenation. It was originally hypothesized that fuel oxygenation may increase Oxy-PAH formation, leading to potential changes in soot structure and composition and helping to provide an explanation for observable changes in soot emissions. Figure 12 presents GCMS derived peak integration counts of Oxy-PAH compounds from solvent extraction of soot filter samples for the four fuel blends of this study. Peak integration counts of Oxy-PAH compounds are observed higher for fuel blends containing dodecane. Evidence suggests that fuel oxygenation from glycerol does not increase concentrations of solvent extractable oxy-PAH compounds.



Figure 12: GCMS derived peak integration counts of oxygenated polycyclic aromatic hydrocarbon (Oxy-PAH) compounds from solvent extraction of soot filter samples for four fuel blends of methane, 0.9 methane + 0.1 dodecane, 0.7 methane + 0.3 glycerol, and 0.65 methane + 0.1 dodecane + 0.25 glycerol by volume.

Emissions Measurements

All gaseous and particulate emissions were collected from the exhaust port of the combustion chamber over a period of 25 minutes at steady state conditions. Soot particulate matter (PM) size distributions are presented in Fig. 13 for each fuel blend in this study. The size statistics were measured via scanning electrical mobility spectroscopy (SEMS) and averaged over a period of 25 minutes at steady state conditions. Particles of aerodynamic diameter 10nm to 50nm typically represent nascent soot particles while particles in the size range greater than 100nm aerodynamic diameter are considered mature soot aggregates. Figure 13 indicates the methane and methane/dodecane fuel blends exhibit a reduced small PM size mode in comparison to methane/glycerol and methane/dodecane/glycerol fuel blends. The distribution of larger mature soot particles is relatively unchanged for all fuel blends. The results stand in contrast to soot samples collected on TEM grids in-situ which showed dramatically reduced particle sizes for methane and methane/glycerol flames. Noting that SEMS size distributions are measured far downstream, it is hypothesized that methane and methane/dodecane soot is oxidized at a greater rate at large HAB and reduced in size by the time the particulate emissions reach the exhaust port of the combustion chamber. Methane/glycerol and methane/dodecane/glycerol particle distributions do not exhibit the same trend. The observations may be explained by a reduction in combustion temperature and oxidation rates due to a reduction in heating value of the oxygenated fuels. Additional in-situ flame diagnostics would be required to test this hypothesis.



Figure 13: Soot particle size distributions from four fuel blends of methane, 0.9 methane + 0.1 dodecane, 0.7 methane + 0.3 glycerol, and 0.65 methane + 0.1 dodecane + 0.25 glycerol by volume. Soot particle sizes are measured via SEMS in the size range 10nm to 500nm aerodynamic diameter.

Figure 14 presents energy weighted PM number emissions from SEMS measurements. Error bars represent the standard deviation of repeatability over a 25-minute test. Pure methane exhibits the lowest PM number emissions, followed by methane/dodecane fuel. Methane/glycerol and methane/dodecane/glycerol fuels exhibit elevated PM number emissions.

Figure 15 shows energy weighted PM mass emissions from SEMS and gravimetric measurements. SEMS derived mass emissions are calculated by correlating aerodynamic diameter (in nm) to TEM derived aggregate volume (in nm³) using the equation $V_p=2.5d_p^{2.1}$ developed from previous work and similar to the approach reported by Park et al. [16]. The resulting aggregate volume distribution is integrated and converted to mass assuming a soot density of 2 g/cm³. Error bars for SEMS derived soot mass represent the standard deviation of repeatability over a 25-minute test. Error bars for the gravimetric data represents the standard deviation of run to run repeatability. Figure 15 clearly illustrates elevated PM mass emissions for methane/dodecane. Furthermore, gravimetric emissions while not quantitively equal to SEMS derived measurements, still corroborate the same general trend in PM mass emissions.



Figure 14: Energy weighted soot particulate matter (PM) number emissions from SEMS measurements for four fuel blends of methane, 0.9 methane + 0.1 dodecane, 0.7 methane + 0.3 glycerol, and 0.65 methane + 0.1 dodecane + 0.25 glycerol by volume.



Figure 15: Energy weighted soot particulate matter (PM) mass emissions from SEMS and gravimetric measurements for four fuel blends of methane, 0.9 methane + 0.1 dodecane, 0.7 methane + 0.3 glycerol, and 0.65 methane + 0.1 dodecane + 0.25 glycerol by volume.

Figure 16 presents energy weighted emissions of oxides of nitrogen (NOx) from FTIR measurements. Error bars represent the standard deviation of repeatability over a 25-minute test. Glycerol is expected to reduce NOx emissions by reducing flame temperature due to its low heating value as an oxygenated fuel. Figure 16 shows that NOx emissions are observed highest for methane while a 10% reduction in NOx is observed for methane/dodecane and methane/dodecane/glycerol fuels. The greatest reduction in NOx (18%) was observed for methane/glycerol fuel.



Figure 16: Energy weighted NOx emissions from FTIR measurements for four fuel blends of methane, 0.9 methane + 0.1 dodecane, 0.7 methane + 0.3 glycerol, and 0.65 methane + 0.1 dodecane + 0.25 glycerol by volume.

Figure 17 presents energy weighted emissions of CO₂ from FTIR measurements. Error bars represent the standard deviation of repeatability over a 25-minute test. CO₂ emissions are in line with a theoretical carbon balance within error bounds, which also serves to validate fuel flow rates and fuel mixture compositions. Methane is widely recognized as the lowest CO₂ emitting hydrocarbon fuel due to its high heating value and molecular structure containing only one carbon atom. Figure 17 shows that CO₂ emissions increase with the addition of dodecane or glycerol, as expected. In fact, glycerol produces the highest energy weighted CO₂ emissions of any fuel component in this study due to its low heating value as an oxygenated fuel.



Figure 17: Energy weighted CO2 emissions from FTIR measurements for four fuel blends of methane, 0.9 methane + 0.1 dodecane, 0.7 methane + 0.3 glycerol, and 0.65 methane + 0.1 dodecane + 0.25 glycerol by volume.



Fuel Blend

Figure 18: Energy weighted CO emissions from FTIR measurements for four fuel blends of methane, 0.9 methane + 0.1 dodecane, 0.7 methane + 0.3 glycerol, and 0.65 methane + 0.1 dodecane + 0.25 glycerol by volume.

Figure 18 presents energy weighted emissions of carbon monoxide (CO) from FTIR measurements. Error bars represent the standard deviation of repeatability over a 25-minute test. For a pure diffusion flame, CO emissions will increase with increasing flame temperature and CO_2 concentration due to dissociation of CO2. Fuel blends of methane and methane/glycerol exhibit the lowest CO emissions while methane/dodecane exhibits the highest CO emissions, generally in line with theory.

Unburned hydrocarbon emissions consisted of only small quantities of methane (approximately 0.5ppm vol/vol) and were effectively unchanged for all fuel blends. Acrolein, a toxic partial oxidation product of glycerol, was also monitored and was determined to be below detectable limits for all fuel blends.

Optical Effects

Previous work has suggested that the absorption and extinction cross sections of soot are dependent on the size parameter $\pi d_p/\lambda$ where d_p is the primary particle diameter and λ the wavelength of light [17]. Smaller particles result in reduced light absorption, with an impact on the visual perception of soot color. The TEM results in this study suggest that the smaller particles formed from methane and methane/glycerol fuel blends may therefore exhibit a reduction in the black color typically visually perceived of soot. This provides some explanation for the observed visual changes to soot filter samples as shown in Figure 6. However, it does not explain the nearly clean filter color of the methane/dodecane/glycerol fuel which exhibited particles sizes similar to methane/dodecane. Theory would instead suggest soot with a similar black color, holding all other factors constant. The analysis is further complicated when accounting for SEMS and gravimetrically derived soot measurements collected from the combustion chamber exhaust. Elevated soot mass and particle size emissions for methane/glycerol and methane/dodecane/glycerol fuels stands in direct contrast to the visual soot loading of filter samples. Evidence therefore suggests that the index of refraction of soot is also impacted by oxygenated fuel blends. Previous work has shown that soot internal structure and organic coatings can have an impact on optical properties [18, 19], which may further explain the visual changes of soot filter samples and changes to index of refraction. Currently, no unifying theory is evident to explain changes in optical properties of soot with changes in fuel blends. Previous work in literature has employed optical diagnostic techniques to determine soot reduction from oxygenated fuels in-situ from combustion chambers and diesel engines [7,8]. Evidence suggests that care should be exercised when employing soot measurements of oxygenated fuels via optical diagnostic techniques assuming a standard soot refractive index.

Conclusions

The objective of this project was to determine the effectiveness of glycerol as a fuel additive to reduce or eliminate soot formation from diesel combustion. Four fuel blends were tested and consisted of pure methane, 0.9 methane + 0.1 dodecane, 0.7 methane + 0.3 glycerol, and 0.65 methane + 0.1 dodecane + 0.25 glycerol by volume. Early visual observations of soot filter samples showed the addition of glycerol to a methane/dodecane fuel blend reduced visible black soot loading to zero. This observation initiated a comprehensive study of the changes in soot emissions for the four different fuels. Soot samples were collected on TEM grids from the flames

of each fuel blend and analyzed via TEM and EDS. Filter samples were collected and weighed for gravimetric emissions measurements. Solvent extractions of soot filter samples were conducted to identify PAH compounds adsorbed on the soot surface. Lastly, continuous emissions measurements of gaseous and particulate emissions were collected for each fuel blend.

TEM data collected at a height of 10mm above the burner surface (HAB) showed that the addition of a significant proportional of glycerol to a methane/dodecane flame did not reduce soot particle aggregate and primary particle sizes significantly. Furthermore, the addition of glycerol to a methane flame did not inhibit soot formation and growth below that of pure methane combustion.

Solvent extractions of soot filter samples indicated that the methane/dodecane fuel blend exhibited the highest PAH concentrations for compounds composed of two to four aromatic rings with an observable reduction in PAH concentrations for larger compounds of four to seven aromatic rings. In contrast, pure methane only exhibited significant PAH concentrations for two of the largest PAH compounds. The addition of glycerol in the methane/dodecane/glycerol fuel blend resulted in a reduction in concentration of smaller PAH compounds in the range of two to four aromatic rings and a subsequent increase in concentration of larger PAH compounds. The addition of glycerol to pure methane also showed an increase in PAH concentrations of larger compounds. Total extractable measured PAH concentration was 10.3ug/g +/- 0.8ug/g for pure methane, 1215ug/g +/- 78ug/g for methane/dodecane, 44.6ug/g +/- 4.6ug/g for methane/glycerol, and 312ug/g +/- 19ug/g for methane/dodecane/glycerol fuel blends.

PM emissions measurements showed elevated PM mass emissions for methane/glycerol and methane/dodecane/glycerol fuels in comparison to pure methane and methane/dodecane. Gravimetric emissions while not quantitively equal to SEMS derived measurements, still corroborate the same general trend in PM mass emissions. The increase in mass emissions for methane/glycerol and methane/dodecane/glycerol fuels was attributed to an increase in size distribution and number concentration of soot particles measured from the combustion chamber exhaust. The results stand in contrast to soot samples collected on TEM grids in-situ which showed dramatically reduced particle sizes for methane and methane/glycerol flames. Noting that SEMS size distributions are measured far downstream, it is hypothesized that methane and methane/dodecane soot is oxidized at a greater rate at large HAB and reduced in size by the time the particulate emissions reach the exhaust port of the combustion chamber. The observations may be explained by a reduction in combustion temperature and oxidation rates due to a reduction in heating value of the oxygenated fuels. Additional in-situ flame diagnostics would be required to test this hypothesis.

Gaseous emission measurements showed NOx emissions were highest for methane with a 10% reduction in NOx for methane/dodecane and methane/dodecane/glycerol fuels. The greatest reduction in NOx (18%) was observed for methane/glycerol fuel. CO₂ emissions were in line with a theoretical carbon balance within error bounds, serving to validate fuel flow rates. Methane is widely recognized as the lowest CO₂ emitting hydrocarbon fuel due to its high heating value and molecular structure containing only one carbon atom. CO₂ emissions increased with the addition of dodecane or glycerol, as expected with the highest energy weighted CO₂ emissions produced by glycerol as a fuel component due to its low heating value

as an oxygenated fuel. CO emissions were lowest for fuel blends of methane and methane/glycerol and highest for methane/dodecane. Unburned hydrocarbon emissions consisted of only small quantities of methane (approximately 0.5ppm vol/vol) and were effectively unchanged for all fuel blends. Acrolein, a toxic partial oxidation product of glycerol, was also monitored and was determined to be below detectable limits for all fuel blends.

TEM, SEMS, and gravimetrically derived soot particles size and mass stand in direct contrast to the visual soot loading of filter samples. Evidence suggests that both changes in particle size and soot refractive index impact optical properties of soot formed from oxygenated fuel blends. Currently, no unifying theory is evident to explain these changes. Previous work in literature has employed optical diagnostic techniques to determine soot reduction from oxygenated fuels insitu from combustion chambers and diesel engines [7,8]. The results of this study suggest that care should be exercised when employing soot measurements of oxygenated fuels via optical diagnostic techniques assuming a standard soot refractive index.

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