

Impact of High Sulfur Military JP-8 Fuel on Heavy Duty Diesel Engine EGR Cooler Condensate

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ABSTRACT

Low-sulfur "clean" diesel fuel has been mandated in the US and Europe. However, quality of diesel fuel, particularly the sulfur content, varies significantly in other parts of the world. Due to logistical issues in various theaters of operation, the Army is often forced to rely on local fuel supplies, which exposes vehicles to diesel fuel or jet fuel (JP-8) with elevated levels of sulfur. Modern engines typically use cooled Exhaust Gas Recirculation (EGR) to meet emissions regulations. Using high-sulfur fuels and cooled EGR elevates problems associated with cooler fouling and corrosion of engine components. Hence, an experimental study has been carried out in a heavy-duty diesel engine running on standard JP-8 fuel and fuel doped with 2870 ppm of sulfur. Gas was sampled from the EGR cooler and analyzed using a condensate collection device developed according to a modified ASTM 3226-73T standard. Engine-out emissions were analyzed in parallel. Analysis of results indicates significantly increased levels of sulfur-dioxide and particulate mass with high-sulfur fuel, but negligible amounts of condensed sulfuric acid under normal operating temperatures.

INTRODUCTION

For logistical reasons, the US military has initiated a *single fuel forward strategy* for its vehicle and aircraft fleets that are stationed and operated in many parts of the world [1]. Currently the single fuel forward is Jet Propellant type 8 (JP-8), a Jet A-1 kerosene-based fuel. When troops are deployed, the military often taps into local fuel supplies in various theaters of operation. In that case, fuel properties may vary through a very wide range. In particular, the sulfur content in some regions is unregulated and may reach extremely high values.

High sulfur content of 3000 ppm or more (on a mass basis) can have an impact on the durability of engine in-cylinder components, engine performance and particulate matter formation [1]. In addition, high sulfur

content affects engine durability due to corrosion caused by the exhaust gas condensate. The corrosion of the heat exchanger in the Exhaust Gas Recirculation (EGR) system is a particular concern on modern engines with EGR. Relatively high amounts of EGR are used for dilution and reduction of combustion temperatures, thus minimizing formation of nitric oxides. However, high mass flow rates of exhaust through the cooler and the presence of particulate matter (PM) in the exhaust lead to fouling of cooler interior walls. Presence of sulfates in soot particles or direct condensation of sulfuric acid has the potential to significantly magnify the corrosion and fouling problems. Sulfates that stick to particulates result from the increased concentrations of SO_2 and SO_3 gas, and sulfurous (H_2SO_3) and sulfuric acid (H_2SO_4). Hence, they are all highly corrosive and a likely reason for corrosion problems observed on some engines [2]. While previous work has identified the problem, additional insight is needed for generating a full understanding about the mechanisms and magnitude of corrosive effects.

Previous research has mostly focused on the effects of high-sulfur JP-8 on combustion and emissions. A JP-8 fuel with 0.2532%wt sulfur was used in a single-cylinder Petter engine by Korres et al. [1]. It was shown that JP-8 can match the performance of diesel by implementing an optimized engine calibration. Yost et al. [3] have shown that the PM-NOx tradeoff curve for JP-8 shifts favorably compared to diesel fuel for a 0-20% range of EGR, but PM emissions increased as sulfur content in the fuel increased. PM emissions have a great impact on exhaust gas visibility, which increases detectability and vulnerability of trucks and tanks on the battlefield.

The objective of this study is to examine the emissions and the composition of the condensate from the EGR cooler of the heavy-duty diesel engine operated with regular JP-8 containing 40 ppm of sulfur. These results were compared to those obtained with JP-8 having a 2870 ppm sulfur content. A special apparatus is designed to sample the exhaust from the EGR cooler,

Report Documentation Page				Form Approved OMB No. 0704-0188	
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1. REPORT DATE 14 APR 2008		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE Impact of High Sulfur Military JP-8 Fuel on Heavy Duty Diesel Engine EGR Cooler Condensate				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Michael Mosburger; Jerry Fuschetto; Dennis Assanis; Zoran Filipi; Heather McKee				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) US Army RDECOM-TARDEC 6501 E 11 Mile Rd Warren, MI 48397-5000				8. PERFORMING ORGANIZATION REPORT NUMBER 18657	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S) TACOM/TARDEC	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) 18657	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES Presented at SAE 2008 World Congress, April 14-17,2008, Detroit, MI, USA, The original document contains color images.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 8	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

and enable separation of solid particles and subsequent controlled condensation of the gas. The temperature control in the apparatus allows independent quantification of the sulfur-dioxide and sulfuric acid present in the exhaust gas. The engine is a Detroit Diesel Series 60, equipped with a variable geometry turbocharger (VGT) and EGR cooler typical of the 2004 generation of heavy diesels.

The paper is organized as follows: the background related to the formation of sulfur oxides and the sulfuric acid is presented first. The description of the experimental setup, including the condensate collection apparatus, is given next. This is followed by the condensate analysis technique for determining the concentration of sulfuric acid and indirect detection of SO₂, and the discussion of results. The paper ends with conclusions and recommendations for a possible extension of the study.

BACKGROUND

THE FORMATION OF SULFUR OXIDES AND SULFURIC ACID

During combustion of fossil fuels, fuel-bound sulfur is converted into sulfur oxides, predominantly into sulfur dioxide (SO₂). A small percentage is further oxidized to form sulfur trioxide (SO₃) [4]. The chemical equilibrium is highly dependent on temperature. The reaction from SO₂ to SO₃ is exothermic and equilibrium favors the formation of SO₃ as the temperature of the exhaust gas decreases. Equilibrium calculations are performed using the following reactions:



SO₃ is corrosive to the materials in the cylinder and downstream in the exhaust manifold. Furthermore it can react with water vapor present in the exhaust stream and form sulfuric acid (H₂SO₄).



If the exhaust gas is cooled below the dew point of water, remaining SO₂ can react with liquid water droplets to form sulfurous acid (H₂SO₃).



H₂SO₃ reacts with oxygen in the exhaust gas to form sulfuric acid.

Both sulfuric acid and sulfurous acid are highly corrosive, which leads to the possibility of reduced component life of the EGR system and intake systems.

Table 1 shows a brief overview of the sulfur oxidation reactions that occur in a combustion engine at different temperatures.

Table 1: Sulfur oxidation steps related to temperature

Temperature	Reaction	Location
2000°C	Mostly SO ₂ , traces of SO ₃	Combustion chamber
<730°C	Equilibrium starts to favor SO ₃ which reacts with water to form H ₂ SO ₄	Exhaust manifold
<165°C	Condensation and deposition of H ₂ SO ₄ starts	Exhaust manifold, EGR cooler, and Intake manifold
<70°C	Water vapor condenses and reacts with SO ₂ to form H ₂ SO ₃	EGR cooler and Intake manifold

Based on the chart, maintaining a higher exhaust gas temperature would:

- Avoid the formation of H₂SO₃ / H₂SO₄ from the reaction of SO₂ with liquid water
- Slow down the oxidation of SO₂ to SO₃ and its subsequent reaction with water vapor
- Avoid the condensation of any H₂SO₄ present in the EGR gas stream

However, this stands in direct contrast to the need to reduce NO_x formation by lowering the combustion temperature, hence the use of cooled EGR and an accompanying increased risk of corrosion. The purpose of our study is to establish methods for measuring sulfur oxides in the exhaust stream, assess the possibility of forming sulfuric acid in the gas stream, and help understand the risk and mechanisms of corrosion in the diesel engine with cooled EGR.

THE IMPACT OF SULFUR OXIDES ON EGR COOLER CONDENSATE

Sulfuric acid is particularly corrosive when it is present in a liquid form and can be deposited on the walls. Thus, the relationship between the heat exchanger temperature and the dew point of H₂SO₄ is very important. However, the dew point of sulfuric acid is difficult to determine since it is strongly correlated to the partial pressure of SO₃. Muller [5] has calculated the H₂SO₄ dew point as a function of SO₃ partial pressure with 10% water content by volume in Figure 1.

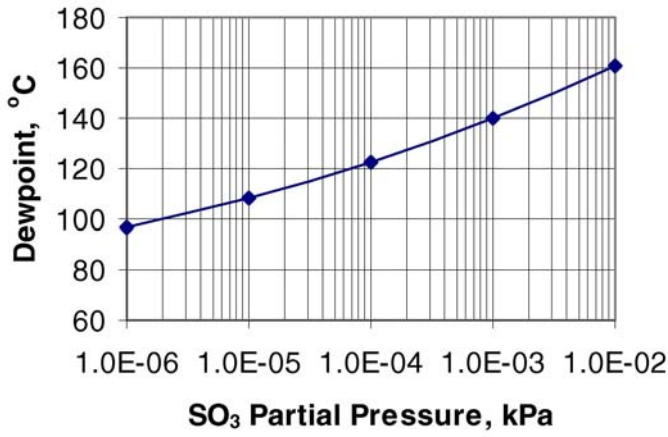


Figure 1: H₂SO₄ dew point vs. SO₃ partial pressure [4]

To demonstrate the impact of SO₃ partial pressure on the sulfuric acid dew point using Muller's [5] calculations, Girard et al. [4] determined temperature values of approximately 122°C for 1 ppm of SO₃ in the exhaust stream, and around 109°C for 0.1 ppm. The SO₃ partial pressure depends on factors such as temperature, sulfur content in fuel, availability of oxygen, and residence time in the exhaust manifold, which is not easy to calculate. Thus, the effect of EGR temperature and other factors on the sulfuric acid concentration and cooler fouling has to be investigated under realistic conditions in a multi-cylinder diesel engine, and that provides the motivation for our study.

SOOT FORMATION AND THE IMPACT OF FUEL SULFUR LEVEL ON PARTICULATE EMISSIONS

Soot particles from diesel exhaust mainly consist of unburned carbon and partially oxidized polycyclic aromatic hydrocarbons (PAH). These particles undergo a simultaneous formation and an oxidation process during the combustion. Obviously, their net release is the difference between formation and destruction. The formation process usually begins with the pyrolysis (high temperature fragmentation without sufficient oxygen) of PAH. They develop from very small precursors of particles to bigger ones through agglomeration with other particles. Ahmad et al. [6] proposed an equation that outlines the different parameters of soot formation:

$$\left[\frac{dm_c}{dt}\right]_{form} = A \cdot T \cdot (HC)^b \cdot (O_2)^{-c} \cdot e^{\frac{-E_{form}}{R \cdot T}} \quad (5)$$

where: A, b, c, and E_{form} are determined experimentally.

This equation shows that soot formation depends directly on fuel, inversely on oxygen, and exponentially on temperature. Thus, the higher the temperature the more soot will be formed. Ahmad et al. [6] however also proposed a correlation for the oxidation of soot:

$$\left[\frac{dm_c}{dt}\right]_{ox} = B \cdot (O_2)^d \cdot e^{\frac{-E_{ox}}{R \cdot T}} \quad (6)$$

where: B, d, and E_{ox} again are determined experimentally.

This equation demonstrates that the oxidation of soot also strongly depends on temperature. The higher the temperature, the more soot can be oxidized. The net soot release is finally described by the difference of soot formation and oxidation:

$$\left[\frac{dm_c}{dt}\right]_{net} = \left[\frac{dm_c}{dt}\right]_{form} - \left[\frac{dm_c}{dt}\right]_{ox} \quad (7)$$

It was found experimentally that soot formation starts at local combustion temperatures between 1500 to 1600 K. If the temperature exceeds around 1900 K, soot oxidation starts to occur rapidly, and for even higher temperatures the net soot release will decrease. Thus, either very low (<< 1500 K) or very high (>> 1900 K) combustion temperatures have to be achieved to lower net soot release from the engine.

Exhausted particles from a diesel engine not only contain organic compounds like PAH, but they might contain traces of metals and sulfates (SO₄⁻²) formed from the sulfur in fuel. Yost et al. [3] investigated the influence of sulfur level in JP-8 fuel on particulate matter and sulfate emissions. JP-8 fuel had been doped with di-tert-butyl-disulfide (DTBDS), to obtain sulfur concentration of 600, 1100, and 2600 ppm. Their experiments were performed on two different engines. In both cases, sulfur concentration in fuel had a strong influence on the emissions of particulate matter. The amount of sulfates trapped in the particles increased with the fuel sulfur concentration. Similar results were found by Hori and Narusawa [7]. Sulfate-containing soot particles can be deposited in the EGR cooler. Contact between the deposits/sulfates in the cooler and condensed water can also produce sulfuric acid in addition to its direct forming from reaction of sulfur oxides with water vapor. It is important to analyze the gas phase and complement that with measurements of the overall level of PM in order to gain insight into the relative importance of either process.

EXPERIMENTAL SETUP

ENGINE

The engine used in this study is a Detroit Diesel Corporation (DDC) Series 60 heavy-duty diesel engine. It is equipped with electronically controlled unit injectors, variable geometry turbocharger (VGT), charge air intercooler, and exhaust gas recirculation (EGR) with EGR cooler. The engine is fully instrumented for measuring pressures, temperatures, and flows. Table 2 gives an overview of the engine specifications.

Table 2: DDC Series 60 Engine Specifications

Total Displacement	12.7 liters
Number of Cylinders	6 cylinders, in-line
Breathing	Turbocharged, intercooled
Fuel Injection	Electronic Unit Injectors
Fuel Pressure	Camshaft Actuated Pump
Bore x Stroke	130mm x 160mm
Compression Ratio	15:1
Rated Torque / Speed	2035Nm / 1200 rpm
Max Power / Speed	250kW / 2100 rpm
Intake Valve Open	26°C CA BTDC
Intake Valve Close	40°C CA ABDC
Exhaust Valve Open	27°C CA BBDC
Exhaust Valve Close	75°C CA ATDC

For the experiments, a military JP-8 fuel was used instead of regular diesel fuel. The baseline JP-8 fuel contains 40 ppm sulfur, has a cetane number of 46.2, a net heating value of 43.356 MJ/kg, and a density of 805.6 g/l [8]. The fuel was doped with di-tert-butyl-disulfide ((CH₃)₃CSSC(CH₃)₃) to 2870 ppm of sulfur. Doping caused a slight increase of cetane number to 47.4, and a slight reduction of density (802.8) and heating value (43.265). Same sets of operating conditions defined by the combination of engine load, speed, EGR flow rate, were visited with both the low-sulfur and high-sulfur fuels.

CONTROLLED CONDENSATION SETUP

A schematic of the controlled condensation apparatus (CCA) setup is shown in Figure 2.

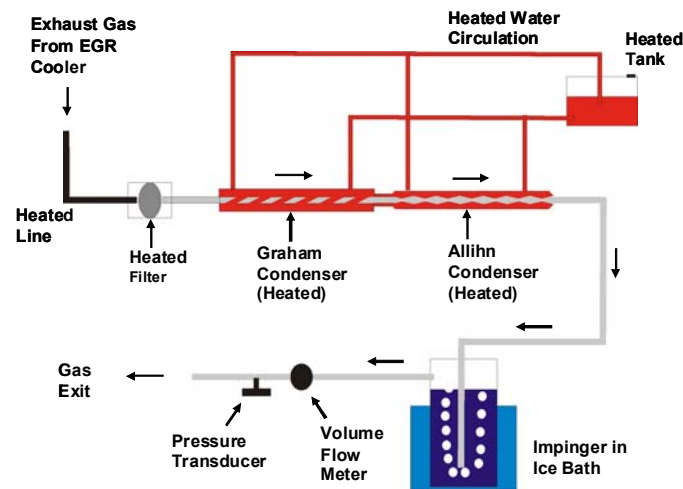


Figure 2: A schematic of the controlled condensation apparatus

A Goksoyr-Ross controlled condensation setup, highly improved by Girard et al. [4] was used to measure SO₃ and H₂SO₄ as well as SO₂ concentrations in the EGR cooler. Findings reported by Kreso et al. [9] were also considered in the design process. A constant sample gas flow is taken directly from the bottom of the EGR

heat exchanger. The gas flows in a loop from the top (inlet) to the bottom (sampling point) and back to the top (outlet). The sample passes through a heated line to a heated stainless steel filter, where any solid particulates contained in the EGR gas stream will be collected. The filter comes with a stainless steel inlet valve to control the flow rate through the whole system. Both the heated line and filter-valve combo are chemically passivated to avoid any reaction of H₂SO₄ with line or filter material. In this section the temperature is kept at 190°C to avoid any condensation of sulfuric acid. After the filter, the sample is flowed through two cooled condensers, the first one being an Graham-type, the second one a Allihn-type condenser. The condensers are kept at a temperature between 75°C and 80°C. Any sulfuric acid contained in the gas stream is expected to condense out and be collected inside the condensers for later analysis. No water must condense out in this section. If it does, SO₂ will react with the condensed water and be erroneously detected as sulfuric acid in the subsequent analysis. Two different condensers were used to double-check collection efficiency. Downstream of the condensers, the gas flows through an impinger filled with a 3% hydrogen peroxide (H₂O₂) solution in water. The impinger sits in an ice bath and is kept at a temperature around 0°C to 5°C. Its purpose is to condense out any water in the exhaust stream. SO₂ is supposed to react with the hydrogen peroxide solution to form sulfuric acid and to be collected in the impinger for later analysis. After the impinger, a volume flow meter together with a thermocouple and pressure transducer measure the mass flow rate over time, for calculation of the total mass flow through the whole setup. A sampling time of 20 minutes for each engine operating condition was experimentally found to be adequate.

SAMPLE ANALYSIS TECHNIQUE

The filter and condensers were rinsed with distilled water after each run. These solutions as well as the hydrogen peroxide solution from the impinger were analyzed to determine the concentration of the collected sulfate ions. It is important to note that any sulfate ions in the impinger originally came from SO₂, whereas sulfate ions collected in the condensers came from sulfuric acid. There are many methods to analyze these samples. Literature recommends either barium perchlorate (Ba(ClO₄)₂) titration or ion chromatography [See Appendix]. However, in our case only one type of ion is expected in the solution, and measurements with a conductivity meter proved to be very effective. Details of the technique based on conductivity are given here, while the other two methods are reviewed in the Appendix for reference.

CONDUCTIVITY METER

A complete chromatography is not necessary if only one type of ion (e.g. SO₄²⁻) is expected in the solutions. In that case, ion concentration can be determined with a conductivity meter. The instrument measures conductance of the solutions being analyzed. It consists

of two platinum electrodes that have a defined surface area and are placed at a precisely defined distance from each other. Both electrodes are inserted into the solution. If voltage is applied to the electrodes, a current can be measured and the conductance can be calculated using Ohm's Law given below:

$$G = \frac{1}{R} = \frac{I}{V} \quad (8)$$

Distilled water has a very low conductance because it contains very few ions. If the amount of ions increases in the solution, the conductance will increase proportionally to ion concentration.

In general the electrical conductance depends on:

- the temperature (increasing temperature leads to increasing conductance due to increased ion mobility)
- the concentration of the dissolved substance
- the valence and mobility of the dissolved substance

Depending on the gap between the electrodes, the supplied voltage, the surface area of the electrodes, and the material of the electrodes, different conductance can be measured for the same solution with different conductivity meters. The measured conductance therefore can not provide information about the absolute ion concentration directly. The instrument needs to be calibrated using sample solutions with known concentrations. A 10 N (Normality) solution of sulfuric acid was diluted down in several steps by a factor of 10 until the detection limit of the conductivity meter was reached. For each concentration the conductance was measured. Using this data, a curve is plotted in Figure 3 and used as a calibration line for determining the ion concentration in unknown solutions.

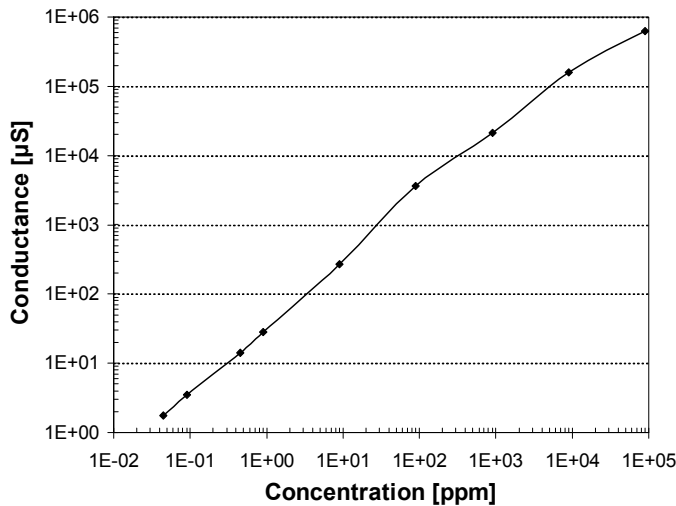


Figure 3: Calibration line for the conductivity meter

To calculate the unknown concentrations of sulfate ions in the solution collected with the CCA sampling setup, a

linear regression was performed. The correlation between conductance and ion concentration was found to be:

$$C_{cal} = 0.0249 \cdot G + 0.4912 \quad (9)$$

DATA POST-PROCESSING

The first step in processing the data is to transform the sulfate ion concentration into total number of ions collected in the sampling solution. This is done by measuring the conductance of a sample, using eq. 9 to obtain the concentration of SO_4^{2-} and then multiplying by the amount of moles in the sample solution to obtain the total number of SO_4^{2-} ions in the solution. Since the sulfate ion concentration in the solution is expected to be negligible, the solution's molar mass is simplified by using the molar mass of water. This is expressed in the following equation:

$$n_{SO_4^{2-}} = C_{cal, SO_4^{2-}} \cdot \frac{m_{H_2O}}{M_{H_2O}} \quad (10)$$

where $n_{SO_4^{2-}}$ is the total amount of ions collected in the sampling solution. This number has to be referenced to the total amount of exhaust gas molecules that passed through the sampling system, and thus the concentration of SO_2 (or analogously H_2SO_4 for the condenser solutions) can be computed by the following equation:

$$C_{SO_2} = \frac{n_{SO_4^{2-}}}{n} \quad (11)$$

Lastly the total number of exhaust gas molecules passing through the CCA (n), is calculated using the ideal gas law. This involves taking measurements with a pressure transducer, thermocouple, and volume flow meter on the outlet of the CCA sampling system. Knowing these three values, the molar flow rate can be calculated using the universal gas constant (R) in the expression:

$$\dot{n}_{fm} = \frac{p \cdot \dot{V}}{R \cdot T} \quad (12)$$

The integration of the molar flow rate ($\dot{n}_{fm}$) over the sampling time results in the total amount of moles that flowed through the CCA system flow meter (n_{fm}).

$$n_{fm} = \int_{t_0}^{t_1} \dot{n}_{fm} dt = \dot{n}_{fm} \cdot (t_1 - t_0) \quad (13)$$

However, the flow meter is mounted at the very end of the apparatus. At this location, all water contained in the exhaust stream has already condensed out and thus a lower volume flow is measured. The concentration of water in the exhaust can be calculated from the known air and fuel flow through the engine, and subsequently used to correct the measured volumetric flow, i.e.:

$$n = n_{fm} \cdot (1 + c_{H_2O}) \quad (14)$$

This completes the derivation of all terms required to calculate the concentration of H_2SO_4 and SO_2 in the condensate from the sampled exhaust gas.

RESULTS AND DISCUSSION

SULFURIC ACID DETECTION

Sulfuric acid was not detected in the condensers under any operating conditions using either the low- or high-sulfur fuel. The likely explanation is that the temperatures and timescales involved in the process do not allow sufficient kinetics-controlled oxidation of SO_2 to SO_3 and subsequent formation of H_2SO_4 . The exhaust gases' residence time between exhaust valve and the EGR cooler might be simply too short. This result was obtained with the engine running at the normal coolant temperature around 87°C . The EGR cooler inlet temperature varied between 210°C to 430°C , depending on the engine load/speed, and gas temperatures at the EGR cooler outlet were in the range of 90°C to 110°C . This finding is quite significant in assessing the overall risk of corrosion. It basically indicates that the fouling with corrosive particulates is much more relevant than direct condensation of sulfuric acid. In addition, there is a possibility of forming sulfuric acid from the SO_2 reacting with condensing water during cold start, or after the engine is shut down. In addition, modifications of the CCA will be considered in order to ensure that even a minuscule amount of the sulfuric acid is detected in the condenser section.

SO_2 CONCENTRATION

Concentration of SO_2 gas is detected indirectly. It reacts with the 3% hydrogen peroxide solution in a glass impinger. The number of sulfate ions detected in the solution is then converted to represent the concentration of SO_2 . Different engine operating conditions were tested with the two fuels (low-S and high-S) and the results are summarized in Figure 4.

As expected, the sulfur concentration in fuel has a very large impact on SO_2 emissions. On average the sulfur dioxide concentrations increase by a factor of about 10 (~7 to 12). While this is very significant, it is far less than the ratio of the sulfur levels in fuel. Obviously, all sulfur is not converted to SO_2 . Instead, large quantities have likely participated in particulate formation, and this possibility will be discussed further in the next section.

The sensitivity of results obtained with the low-S fuel to operating conditions is low. The concentration of SO_2 obtained with the high-S fuel (2870 ppm S) is most sensitive to engine load. The SO_2 concentration increased from 32.9 ppm to 44.4 ppm when engine load was changed from 20% to 50%. The reason for this is the richer mixture at higher loads, as A/F ratio dropped from 51.6 at 20% load, to only 27.6 at 50% load.

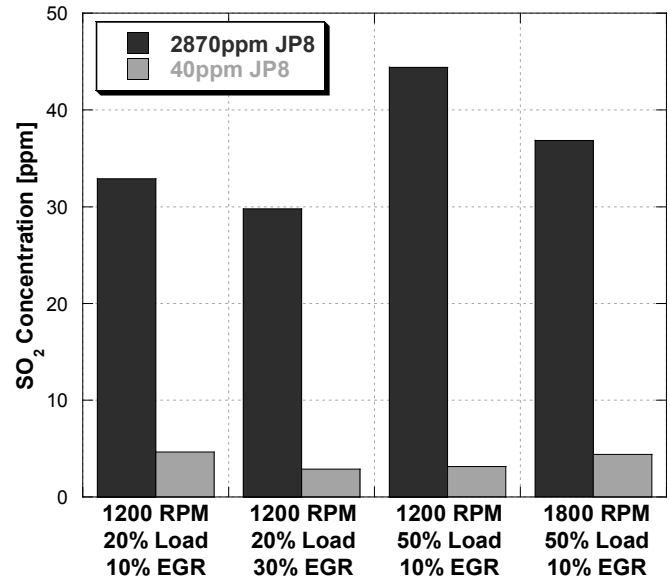


Figure 4: SO_2 concentrations in the exhaust gas sampled from the EGR cooler inferred from the analysis of the condensate formed in the impinger chamber. Engine coolant temperature was 87°C .

PARTICULATE MASS IN THE EXHAUST

A heated and passivated stainless steel particulate filter was used to capture particulate matter in the engine exhaust. The filter with captured particulates was then submerged in distilled water to try to create a reaction between sulfates absorbed into PM and water. However, subsequent analysis of the water solution provided inconclusive results. Apparently the sulfate concentrations were too low for the accuracy level of the conductivity meter and an alternative technique will be needed in future investigations.

Nevertheless, NOx-PM tradeoff obtained previously in the same engine with low- and high-sulfur fuels support the hypothesis that a large amount of sulfates is attached to particulates. Figure 5 shows that the tradeoff curve moves significantly in the direction of increased PM concentrations when engine runs with the high-sulfur fuel. The individual points correspond to different levels of EGR, and mass of particulate matter was measured using a mini-dilution tunnel and filter paper [8]. The increased amount of sulfates in the exhaust explains the disproportionately small increase of SO_2 in the exhaust of the engine running with high-sulfur fuel. It also indicates that the main risk of corrosion comes from the EGR cooler fouling, and possible

forming and absorption of the sulfuric acid in the deposits during cold-start or after engine shut-down. Refinements of the diagnostics techniques, particularly the analysis of the particulate composition, will be necessary to fully confirm this finding.

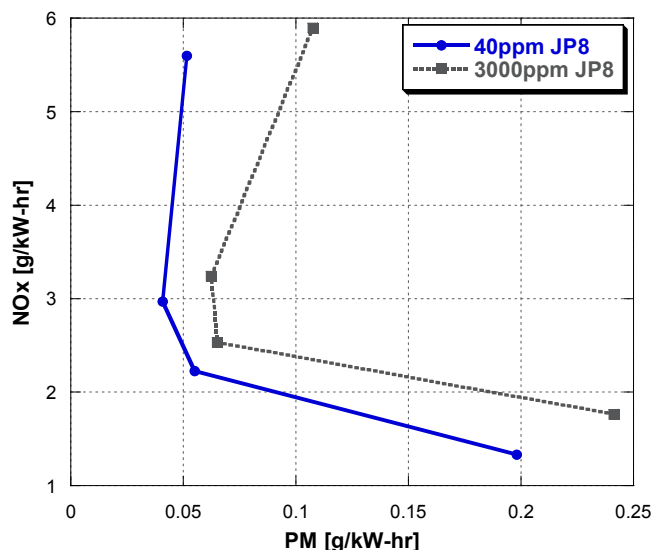


Figure 5: Comparison of NOx - PM tradeoff curves obtained with low- and high-sulfur fuels. Each point corresponds to different levels of EGR at 1200 rpm and 20% load [8].

CONCLUSION

The purpose of this study was to examine the impact of high sulfur JP-8 fuel on the corrosive properties of the condensate from the EGR cooler in a heavy-duty diesel engine. A controlled condensate collection apparatus was designed and set up for this purpose. It allowed separation of the solid particles from the gas, and subsequent detection of the presence of sulfuric acid or sulfur-dioxide in the exhaust sampled from the EGR heat-exchanger. The concentration of sulfuric ions in the water-solution was inferred from measurements with a conductivity meter.

Sulfuric acid was not detected in the condensers when the engine was running at a normal coolant temperature ($\sim 87^{\circ}\text{C}$) using either the low- or high-sulfur fuel. The likely explanation is that the temperatures and timescales involved in the process do not allow sufficient kinetics-controlled oxidation of SO_2 to SO_3 and subsequent formation of H_2SO_4 .

The sulfur concentration in fuel has a very large impact on SO_2 emissions. On average the sulfur dioxide concentrations increased by a factor of about 10 when sulfur content in fuel increased by 70 times. Obviously, all sulfur is not converted to SO_2 . Of all operating conditions considered, engine load (and thus A/F ratio) had the most influence on absolute levels of SO_2 .

A heated and passivated stainless steel particulate filter was used to capture particulate matter in the engine exhaust. The filter with captured particulates was then submerged in distilled water to try to create a reaction between sulfates absorbed into PM and water. However, subsequent analysis of the water solution provided inconclusive results. Apparently the sulfate concentrations were too low for the accuracy level of the conductivity meter.

Concentration of particulate mass in the exhaust increased significantly when the engine was operated with high-sulfur fuel. This can be attributed to increased amount of sulfates in the soot particles, and it provides the likely explanation for the disproportionately small increase of SO_2 in the exhaust of the engine running with high-sulfur fuel. It indicates that the main risk of corrosion comes from the EGR cooler fouling, and possible forming and absorption of the sulfuric acid in the deposits during cold-starts or after engine shut-down. Refinements of the diagnostics techniques, particularly the analysis of the particulate composition, will be necessary to fully confirm this finding.

ACKNOWLEDGEMENT

The authors wish to acknowledge the technical and financial support of the Automotive Research Center (ARC) and the U.S. Army Tank-Automotive Research, Development and Engineering Center (TARDEC). The ARC is a U.S. Army Center of Excellence for Automotive Research at the University of Michigan, currently in partnership with the University of Alaska-Fairbanks, Clemson University, University of Iowa, Oakland University, Virginia Tech University, and Wayne State University. Gerald Fernandes is acknowledged for providing the measurements of the particulate mass in the exhaust.

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

G = Electrical conductance

R = Electrical resistance

I = Electric current

V = Voltage

C_{cal} = Sulfate ion concentration [ppm mol]

G = Electrical conductance [μ S]

$n_{SO_4^{2-}}$ = Total number of sulfate ions [mol]

$C_{cal, SO_4^{2-}}$ = Concentration of sulfate ions [-]

m_{H_2O} = Total mass of H₂O solution [g]

M_{H_2O} = Molar mass of H₂O [18 g/mol]

C_{SO_2} = Concentration of SO₂ in exhaust gas

C_{H_2O} = Concentration of H₂O in exhaust gas

N = Normality (Number of moles of a solute dissolved in a liter of solution [mol/l] times number of protons exchanged per molecule)

n = Total number of molecules passed through the sampling apparatus

p = Gas pressure [Pa]

$\dot{V}$ = Volume flow rate [m³/s]

$\dot{n}_{fm}$ = Gas quantity flow at flow meter

$\bar{R}$ = Universal gas constant [8.314 J/mol*K]

T = Temperature [K]

t₀ = Starting time

t₁ = End time

APPENDIX

Three candidate techniques for measuring concentration of the sulfate ions in the collected solution were identified. Namely, barium perchlorate (Ba(ClO₄)₂)

titration, ion chromatography, and measurements of conductivity. The conductivity meter was used in this study, as it provided sufficient accuracy combined with relatively straight-forward implementation. The application of the conductivity-based methodology was enabled by the fact that we expect only one type of (sulfate) ions in the solution. Nevertheless, details of the titration technique and ion chromatography are given here for reference.

BARIUM PERCHLORATE TITRATION

Barium perchlorate titration belongs to the group of color change titrations. A few droplets of the indicator Thorin (C₁₆H₁₃AsN₂O₁₀S₂) are added to the analyte, turning the color of the solution from colorless to yellow. The sulfuric acid in the analyte is ideally completely dissolved in its ions H⁺ and SO₄²⁻. When adding barium perchlorate solution, the barium perchlorate dissolves into its ions Ba²⁺ and ClO₄⁻. The Ba²⁺ ions will immediately react with the SO₄²⁻ ions and form barium sulfate salt (BaSO₄), which is insoluble and precipitates as a white sediment. However, if no more SO₄²⁻ ions are available, the Ba²⁺ ions and thorin indicator start to form a red barium-thorin complex. At exactly this point, when no more SO₄²⁻ is available, the solution starts to change its color from yellow (thorin) to red (barium-thorin complex). The color change indicates that the endpoint is reached, and the adding of barium perchlorate is stopped. By measuring the exact amount of Ba(ClO₄)₂ added, the amount of SO₄²⁻ ions that reacted with the barium can be calculated and thus the original amount and concentration of sulfuric acid can be determined. Color-change titration using the barium perchlorate is in principle very precise. However, the point where the solution changes its color has to be detected very accurately, and doing it by naked eye is difficult. Since we expect the SO₄²⁻ concentration to be very low, optical measuring devices would have to be used to ensure sufficient precision.

ION CHROMATOGRAPHY

In ion chromatography, different columns of ion-exchange resins can be used to separate either cations (positive charge) or anions (negative charge) from each other. These resins basically consist of an insoluble structure in the form of small beads, fabricated from an organic polymer substrate. The sites on its surface can easily trap or release certain ions. The specific type of the resin is chosen depending on the ion of interest. Cations can only be separated on a cation exchange resin (Catex), anions only on a column using an anion exchange resin (Anex). On the bottom of the column is a detector cell. The detector must be able to see or measure sample ions in the presence of the eluent ions. However, performing a full ion chromatography is very time intensive due to the large number of sample solutions that are to be analyzed.