Oxidative Reactivity of Gasoline Direct Injection (GDI) Particulate for E0 and E30 Blends of Ethanol in Gasoline

ENGINEERING

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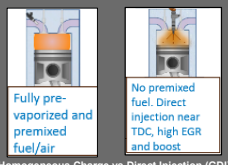
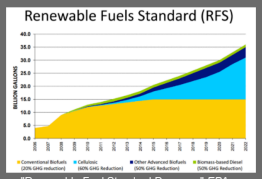
Motivation:

Gasoline Direct Injection (GDI) engines have penetrated the automotive market due to their increased fuel efficiency and high power output. However, due to incomplete fuel volatilization and partially fuel-rich zones, GDI engines tend to produce more particulate matter than compared to conventional spark ignition engines. To aid in reducing PM, GDI engines could benefit from a particulate filter. However, adding a filter in the exhaust system is known to increase backpressure, which is especially problematic for GDI operation and can lead to a fuel penalty. To efficiently regenerate a Gasoline Particulate Filter (GPF), the reactivity of GDI particulate matter must be understood. Previous work has shown that diesel particulate matter formation, nanostructure and reactivity is a function of fuel type. With ethanol being the leading and currently deployed biofuel for gasoline engines, there is interest in studying the effect it has on GDI PM reactivity.



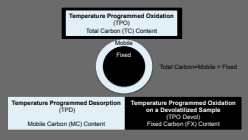
Homogeneous Charge vs Direct Injection (GDI)
Adapted from McCormick, Robert "Biobiend stocks that Enable High Efficiency Engine Designs" (2016)



"Renewable Fuel Standard Program." *EPA*.

Goal:

Investigation of the kinetics and mechanism for the oxidative reactivity of GDI particulate and the effect of ethanol blending on the reactivity and structure.



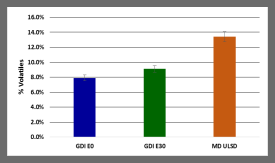
Approach:

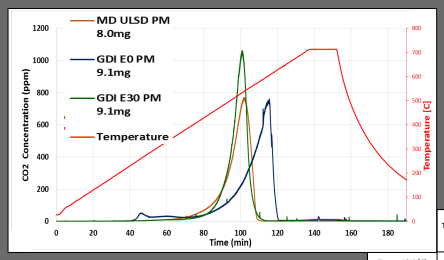
Using the CRCL Microreactor (left) and Hiden QGA Mass Spectrometer :

- Quantify the relative fractions of volatile and fixed carbon by Temperature Programmed Desorption (TPD)
- Examine the effective oxidation rates by Temperature Programmed Oxidation (TPO) in 20% O_2, 10% H_2O with balance Ar.
- Measure the Arrhenius kinetics by Isothermal Pulsed Oxidation (IPO) and study how they change with extent of reaction.
- Investigate total specific surface area by flowing BET in order to understand the nature of the physical structure of the samples and how they change with extent oxidation.

Results:

Likely due to the higher volatility of ethanol and gasoline hydrocarbons, both the E0 and E30 PM samples were found to have lower volatile fractions as compared to MD-Diesel PM. These were measured by TPD to 600°C in Ar.



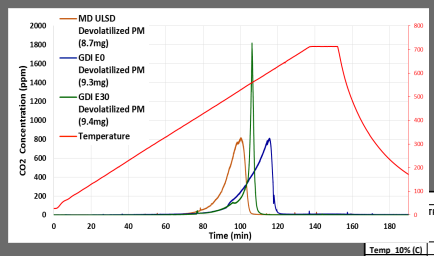


The TPO comparison shows that the E30 PM is more reactive and the E0 PM is less reactive than the MD-Diesel PM.

The table compares the temperatures, measured in the sample bed at several conversions.

	TPO MD ULSD PM (8.0mg)	TPO GDI E0 PM (9.1mg)	TPO GDI E30 PM (9.1mg)
Temp_10% (C)	452	381.8	461.3
Temp_50% (C)	530.4	552.9	516.8
Temp_75% (C)	548.2	581	529.2
Temp_95% (C)	563	596.7	539.8
Temp_Peak (C)	545.7	605	528.9

TPO of the fixed carbon from the three PM samples shows that once the volatiles are removed, the samples become less reactive than their nascent counterparts. The E30 is notable, because it reacts in very narrow peak.



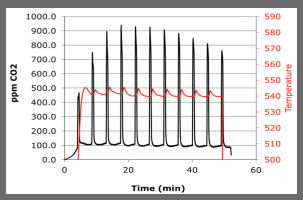
We believe that this indicates that the nano-structure is uniform and has been strongly influenced by the ethanol. It is likely comprised of short, curved lamellae. HR-TEM would confirm this hypothesis.

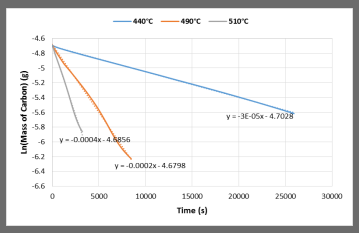
	Sample		
	TPO Devol MD ULSD PM (8.7mg)	TPO Devol GDI E0 PM (9.3mg)	TPO Devol GDI E30 PM (9.4mg)
Temp_10% (C)	470.2	499.5	480.7
Temp_50% (C)	527.2	561.5	552
Temp_75% (C)	541.2	583.1	558.2
Temp_95% (C)	553.2	597	569.1
Temp_Peak (C)	544.5	599.4	556.8

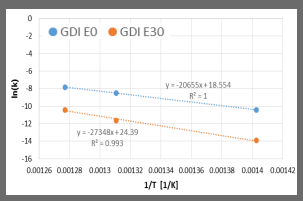
The kinetic data is not yet complete, we are presenting work in progress.

Differential, isothermal pulsing was used to determine the kinetic parameters. Four temperature (440°C, 490°C 510°C, and 540°C) were chosen based on the TPOs.

A first order plot for three of the E0 IPO experiments is plotted below. Calculating an average k value for each, and doing the same for the E30 samples, we are able to create a preliminary Arrhenius plot (middle right plot). From this plot, the activation energies are calculated to be 171.7 kJ/,ol for E0 and 227.4 kJ/mol for E30.

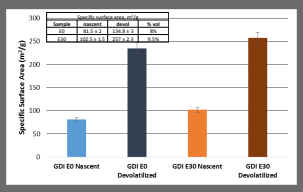


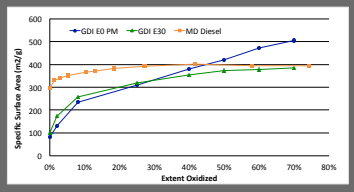




Previous work on PM from ULSD and Biodiesel showed the importance of the surface area available for reaction. In the plot at right, we see the expected trend of increasing surface area with removal of the volatiles and that the E30 PM has greater surface area for both nascent and devolatilized samples as compared to the E0.

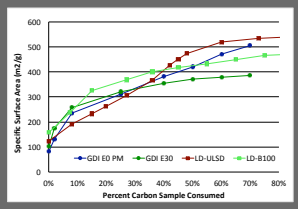
We also made BET measurements at several points along the reaction to track surface area evolution. We see that for both samples, the surface area continues to grow as PM is oxidized.





It is interesting that the E30 initially has higher surface area than the E0, until there is cross over between 30 and 40% oxidation.

This is similar to what was seen for light-duty particulate samples from ULSD and B100.



Future Work:

- Finish analysis of additional temperatures for Isothermal experiments for both PM samples.
- Investigate whether reactivity is changing over the course of the burnout – and if there should be k values defined by burnout segment.
- Transmission electron microscopy (TEM) could verify the physical difference in the nanostructure
- Publish paper

Summary:

The effect of fuel type was investigated by studying the bulk oxidative reactivity of the nascent and devolatilized PM by TPO, quantifying the volatile content by TPD, measuring the surface area with extent of reaction by BET, and determining the kinetic parameters with IPO. Further work is ongoing to include more temperatures for the IPOS and to

Conclusions to Date:

GDI E30 PM is more reactive than Diesel PM, which is in turn more reactive than GDI E0 PM. The differences in effective reaction rates come from physical differences in the carbon nanostructure. It is likely that ethanol has an effect on how GDI PM is being formed in cylinder, similar to what has been seen for other biofuels. We suspect that GDI E30 PM is composed of shorter carbon lamella than E0.

References

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