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Study of Graphite Oxide and Graphene as Enhancers for NATO F-76 and Biofuel

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EXECUTIVE SUMMARY

Project Summary

The aim of this project was to test the performance of Graphite Oxide (GO) and Graphene (G) as fuel additives. Both compounds are variations of the honeycomb structure found in graphite but possess higher surface areas and different amount of oxygen functional groups. The use of Graphite Oxide was considered due to its ability to release the oxygen species at moderate temperatures, while Graphene could be readily dispersed and completely burned off during the combustion process.

Graphite oxide was fabricated by chemical routes and graphene by thermal exfoliation. X-ray powder diffraction was used to characterize the crystal structure of the initial powders and the particulate sizes were studied by scanning electron microscopy.

The additives were mixed with NATO F-76 diesel fuel in 0.1 to 3 % wt ratios and with 0.01 % wt of biofuel. The mixtures were then analyzed by differential scanning calorimetry and thermogravimetry to determine heat flows and mass changes as the samples were heated, then compared with bare F-76 or bare biofuel. The evolved gases from all the processes were identified by mass spectroscopy.

The fuel-additive mixtures were tested in a diesel engine to determine ignition delays and the cetane numbers for each composition are reported.

Background

During 2009 the Secretary of the Navy (SECNAV), set forth five DON energy goals to be reached by the year 2020; the goals aim to reduce the DON's environmental fingerprint and increase its energy independence [1]:

- Energy Efficient Acquisition: Evaluation of energy factors will be mandatory when awarding contracts for systems and buildings.
- Sail the "Great Green Fleet" [2]: DON will demonstrate a Green Strike Group capable of using advanced biofuel blends, nuclear power, and employing energy saving methods in local operations by 2012 and sail it by 2016.
- Reduce Non-Tactical Petroleum Use: By 2015, DON will reduce petroleum use in the commercial fleet by 50%.

- Increase Alternative Energy Ashore: By 2020, DON will produce at least 50 % of shore-based energy requirements from alternative sources. These include, but not limited to, sources such as wind, solar, geothermal, wave energy, tidal currents, nuclear energy, and biofuels derived from algae, camelina, and other feedstocks [3].
- Increase Alternative Energy Use DON-Wide: By 2020, 50% of total DON energy consumption will come from alternative sources (see previous bullet).

Regarding the production and use of "alternative sources" stated in the last two energy goal bullets previously mentioned; such alternative sources "must be 'drop in' replacements, able to mix with traditional petroleum products with no adverse effects to the fuel quality." Furthermore, the DON mandates alternatives have lower lifecycle greenhouse gas emissions than conventional petroleum-based fuels. These requirements added to the motivation to study GO and G as drop-in additives to F-76.

Regarding alternative sources:

While the SECNAV mandates that alternative sources must be drop-in replacements, there are considerations that the DON must overcome in order to transition into a more energy efficient entity amongst petroleum users in the world. Among these considerations include technology maturity, resource availability, and alternative fuel availability. As technology matures, the DON must leverage leading-edge advances in technology and deploy them in the tactical and shore arenas [3] .

Thus far, research into alternatives has included the Green Hornet flight [3,4], the Great Green Fleet demonstration [2], and studies involving additives in thermite mixtures [5] among others. Earth Day 2010 marked a significant milestone in fuel alternative studies as the DON successfully launched a F/A-18 Super Hornet using a 50/50 blend of conventional jet fuel and a biofuel derived from camelina (a hardly U.S.-grown plant that can thrive in the harshest of soils). The 50/50 blend made absolutely no difference in performance of the fighter, which displayed its capabilities at speeds including supersonic. During the July 2012 Pacific Rim exercise, the largest international maritime warfare exercise, United States' participants, which included an aircraft carrier and its air wing, a cruiser, two destroyers, and an oiler, (nicknamed the 2012 Great Green Fleet), demonstrated successful performance of drop-in replacement advanced biofuel blend (50/50 blends made from algae mixed with petroleum: HRD-76 and HRJ-5) and other energy efficient technologies in an operational setting. All systems met operational tempo requirements.

Lastly, the Mechanical Engineering Department at the Naval Postgraduate School (NPS) has researched drop-in additives (graphite oxide (GO) and graphene (G)) in solid propellants to study thermite reactions. Conclusions from research showed significant increases in exothermic reactions when compared to the solid propellants without the additives [5] . The next step is to consider these two additives in fuels used by the DON.

Findings and Conclusions

Graphite oxide (GO) and graphene (G) were successfully prepared in the laboratory. GO was synthesized by oxidation of graphite, while G was prepared using thermal exfoliation of GO. X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques were employed to verify their crystalline structures and their particle size and distribution, respectively. Calorimetric characteristics were studied using a Differential Scanning Calorimeter (DSC) while their mass reduction was determined using ~~a~~ Thermogravimetric Analyzer (TGA) as these parameters were exposed to slow burning-rates in an air environment. Evolved gases from the TGA/DSC experiments were analyzed using a Mass Spectrometer (MS).

Using NATO F-76 diesel fuel as the basis fuel, GO and G additives were mixed with the fuel in quantities from 0.1 wt% up to 3.0 wt%. For comparison with F-76 neat, their thermal behavior was also studied using DSC, TGA and MS. It was found that in all GO-mixed fuels (0.1, 1, 2 and 3%), energy output during combustion at slow burn-rates improved over that of F-76. For the G-mixed fuels the results were less consistent, showing improved energy output only for samples with additives in 0.1 and 2%. TGA for all mixtures showed a complete weight loss in a single step for all samples. The MS analysis showed that the mass loss observed was related to water and carbon dioxide Conclusions from these studies indicate that 0.1wt% GO and G mixtures should be studied further in practical combustive reaction settings and compared to F-76. Those samples contain the minimum amount of additive but still showed an increase in the heat flows measured when compared to legacy fuel.

Preparation of 1.5-liter quantities of 0.1wt% GO/F-76, 0.1wt% G/F-76 mixtures, and F-76 neat were done to conduct analysis of cetane number, gross heat value, and net heat of combustion. Through a high burn-rate process, data showed there was no conclusive evidence of changes in any of these parameters against F-76.

Studies were also conducted on biofuel, Hydrogenation-Derived Renewable Diesel (HRD) with only 0.01 wt% of GO and G as additives; results showed that Graphene has the potential to increase the cetane number of mixtures.

The F-76 GO and G mixtures' performance were also studied in a practical setting, namely, using a Detroit 3-53 marine diesel engine. Of note, it was found that the fuel/water separator on the engine was separating an unknown amount of the additives from the fuel/additive mixtures, when pumped from the sample mixture tank, though the fuel in the engine's gravimetric measurement holding tank still contained some additive. Parameters measured included: cylinder pressure, start of injection (SOI), maximum rate of release (MRR), oxygen content (lambda value) of exhaust gases, heat of release relating to energy output, and ignition delay. Findings:

- Slight increases in peak pressure (PP) for both GO-mixed and G-mixed fuels over F-76, relating to the possibility of higher heat releases, while the angle of peak pressure (AOP) changes were minimal.
- Decreased MRR for both GO-mixed and G-mixed fuel over F-76, relating to more complete combustion cycles and decreasing the likelihood of engine knocking.
- Consistent SOI points around 14° before TDC and consistent strain inside the cylinders for the enhanced fuels and F-76, relating to decreased likelihood of injection problems and thermal damage inside the cylinders.
- There were no differences found in the heat of releases or start of combustion points for either of the additive mixtures against F-76 at either 1100 or 1700 RPM.
- Decreased lambda values for both GO-mixed and G-mixed fuels over F-76 when compared at the same speeds and torques, and decreased lambda values as speed and

torque increased overall. This relates the possibility of more complete combustion inside the cylinders.

- As there were no differences in heat of release or SOC, the ignition delay for both additive mixtures were similar to that of F-76.

Recommendations for Further Research

Future work is recommended in two areas. The first is with the experimental setup. We had issues with the GO and G separating in the fuel/water separator. An evaluation of the diesel engine setup should be done to determine a more appropriate method of fuel injection to fully evaluate the potential of using these additives.

Second, the quantity of the fuel samples in which this study used was minimalistic. Larger quantities (gallons) should be created in order to obtain many cycles of data in the diesel engine to further develop data, which could better represent the potential of these additives.

The use of grater graphene additive weight percentages in biofuel mixtures is recommended for future research, given that the small (0.01) wt% used in the present study showed an increase in cetane number.

References

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