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**EFFECTS OF ENVIROFUELS DFC ON
REDUCING COMBUSTION EMISSIONS**

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This document is a summary of the research, development and testing performed by us on EnviroFuels Diesel Fuel Catalyzer (DFC), fuel-borne technology that have been demonstrated effective in reducing environmentally damaging emissions accompanying combustion of petroleum fuels in internal combustion engines. This research has provided an understanding of the effects of DFC and its underlying mechanisms, leading to the improvement of the product formulation, and providing a basis for successful field tests of performance. While this paper is necessarily technical, we attempt to address an audience with a general scientific or engineering background.

INTRODUCTION

The acquisition in 2002 by EnviroFuels, L.P. (EnviroFuels) of technology developed by MDEChem was based upon impressive tests of energy efficiency and emissions reductions due to, according to U.S. Patent 5,540,788, the formation of iron-phosphate conversion surfaces through contact of the metal surface with the additive formulation in lubricant.

Our laboratory investigations (White Paper 1) have demonstrated the nature of the complex phosphate surface, and the mechanisms underlying its formation, resulting from contact of EnviroFuels DFC product components with Fe and Al alloys.

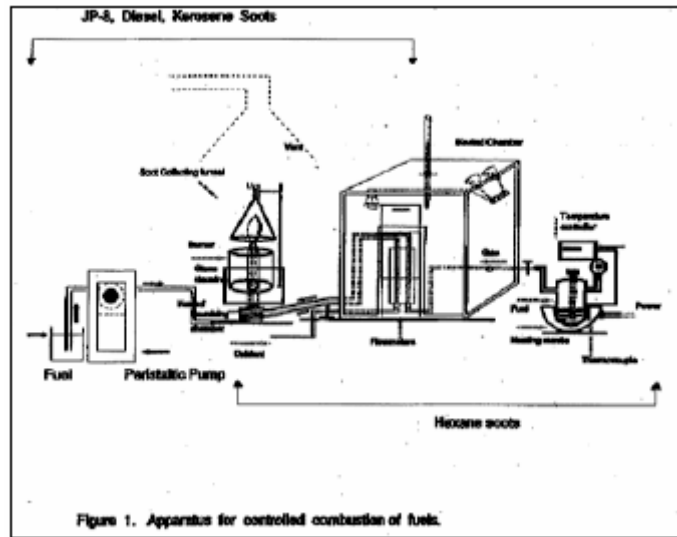
Recognizing that combustion chemistry is a type of plasma chemistry involving the reactions of molecular fragments and radicals at high temperature, unrelated to the chemistry of conversion surface formation from lubricant additive, we sought to determine whether reported pollutant reduction as well as increased fuel efficiency could be attributed to surface phenomena. To do so, we examined the nature of the surfaces formed by combustion of fuel with and without the product DFC.

EFFECT OF DIESEL FUEL COMBUSTION ON METAL SURFACES

Utilizing an apparatus for controlled combustion, **Figure 1**, we subjected the polished surfaces of 1018 steel cylinders to the combustion plume of diesel fuel (Total Petroleum) and the same fuel containing DFC at an additive concentration corresponding to an estimated phosphorus (P) concentration of 45 ppm. The metal surface temperature averaged about 2000 °F during these trials.

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Figure 1



Electron spectroscopy experiments reveal the difference between the effects of combustion and surface chemistry on the metal surface. **Figure 2** is a scanning electron micrograph (SEM), at high resolution (2000X), of the steel surface impacted by the flame from the combustion of diesel fuel containing the additive for a period of 9 hours at a high air/fuel (A/F) ratio (lean combustion). Adjoining the SEM in **Figure 2** is an energy dispersive Xray fluorescence spectrum, revealing the presence of P and K in approximately 1 μ m nodules uniformly distributed over the SEM field which is dominated by iron oxide surface, revealing the nature of the active ingredients in the combustion flame. This spectrum resulted from focusing on one of the microscopic nodules, all of which produced qualitatively the same spectrum. At lower resolution, only the components of the steel (Fe, O, Mn) can be observed as shown in **Figure 3**.

The components of the product appear to be constrained to these microscopic nodules resulting from the combustion plume. To the extent that the product DFC in the fuel contributes to decreased pollutant emission and increased fuel efficiency, it seems unlikely that this kind of surface is responsible. Rather, the role of the active component(s) of the product would seem to rest in fuel combustion phenomena.

Figure 2

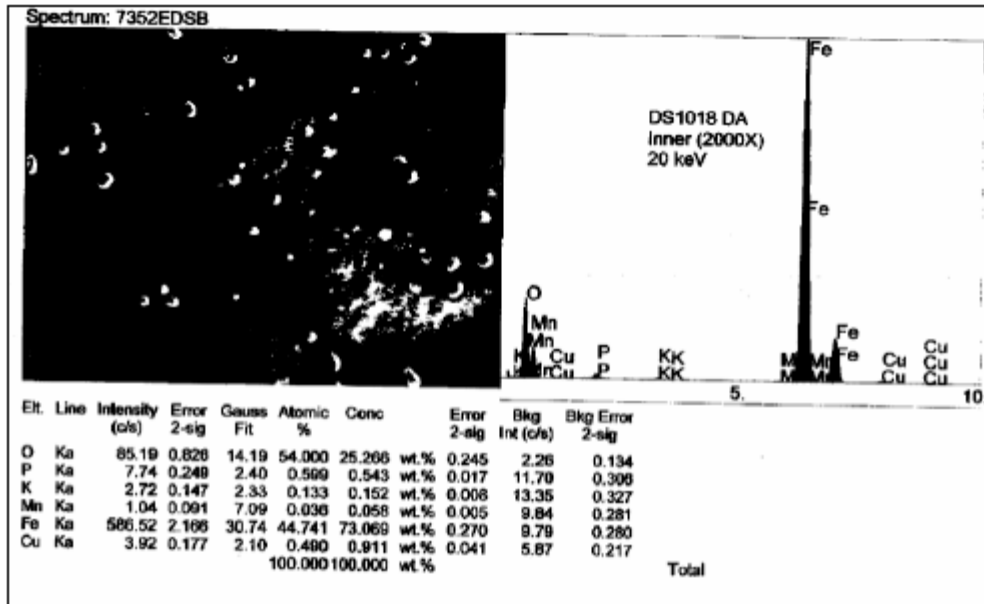
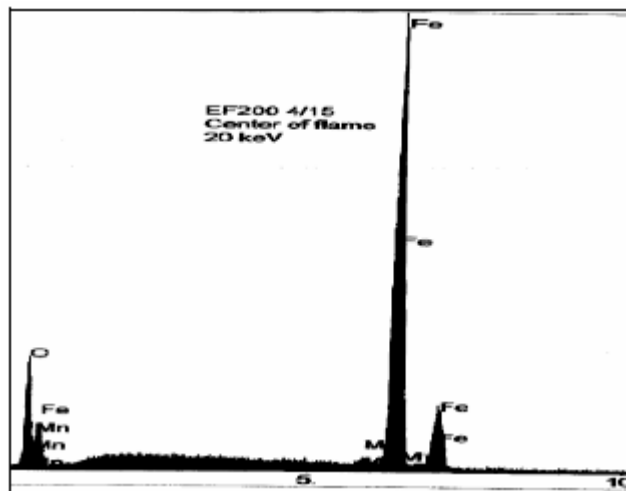


Figure 3



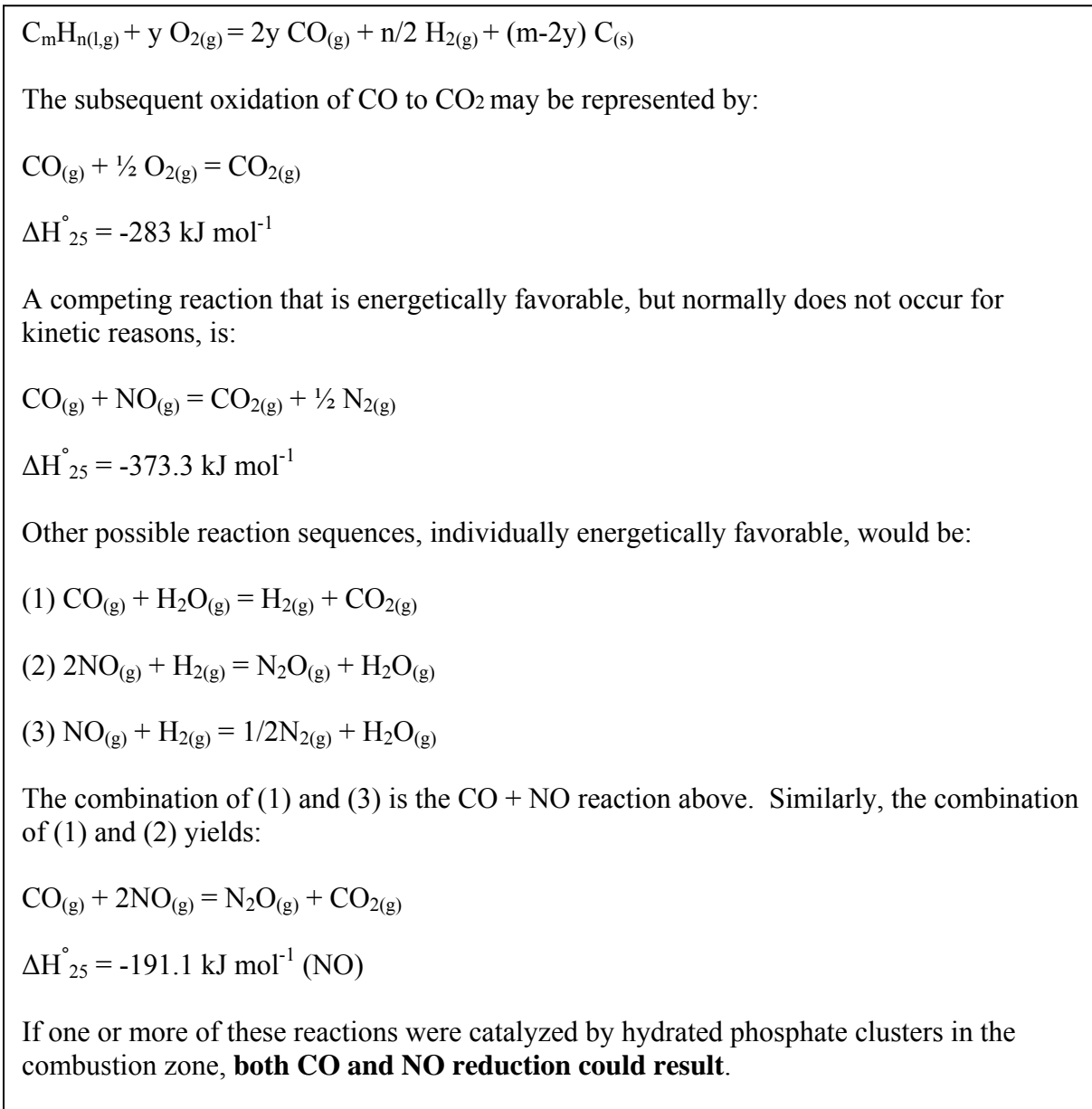
EFFECTS OF THE ADDITIVE ON PETROLEUM FUEL COMBUSTION

One reasonable hypothesis for the effectiveness of the product would be the behavior of fine phosphate-containing clusters, nucleated from dispersed phosphate species in the fuel, stable at high temperatures, behaving as micro heterogeneous catalysts in reactions leading to the oxidation of CO, particulate and NO, and thus their diminution as combustion products. Reductions in CO and particulate alone would result in higher fuel efficiency through reactions not normally observed in the combustion plume. Some of these reactions, unobserved in the absence of catalysis, are energetically favorable as summarized in **Figure 4**.

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The formation of CO through incomplete combustion may be represented by the generalized equation:

Figure 4



Pollutant Emission

On the basis of this heterogeneous catalysis hypothesis, we have carried out an extensive series of tests on the effect of product DFC on emissions from diesel fuel combustion. Specific pollutant species whose emission has been measured are CO, NO, SO₂, and particulate. In this paper we shall describe the results obtained with low sulfur (0.041%) diesel fuel and describe the methods of measurement employed.

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Carbon Monoxide

Carbon monoxide emission was measured by infrared spectroscopy, specifically with FTIR, using a spectroscopic gas cell interfaced with the combustion apparatus through a particle filter and water absorption train. These experiments required a modification of the combustion apparatus (**Figure 1**) as diagrammed in **Figure 5**. Measurement of CO was at its 2143 cm^{-1} absorption, while confirmatory spectra of CO_2 at 2350 cm^{-1} , 3610 cm^{-1} , and 3715 cm^{-1} were obtained as well. **Figure 6** is the FTIR spectrum of the diesel combustion plume, with and without additive. In **Figure 7** is shown the expanded CO spectrum centered at about 2143 cm^{-1} . While the spectra are illustrative of the reduction in CO emission by the product, repeated trials have yielded reductions averaging $74\pm 13\%$. A concomitant increase in CO_2 emission results from the decrease in CO, as most easily observed in the relative sizes of the CO_2 combination bands at 3610 cm^{-1} and 3715 cm^{-1} in **Figure 6**.

Figure 5

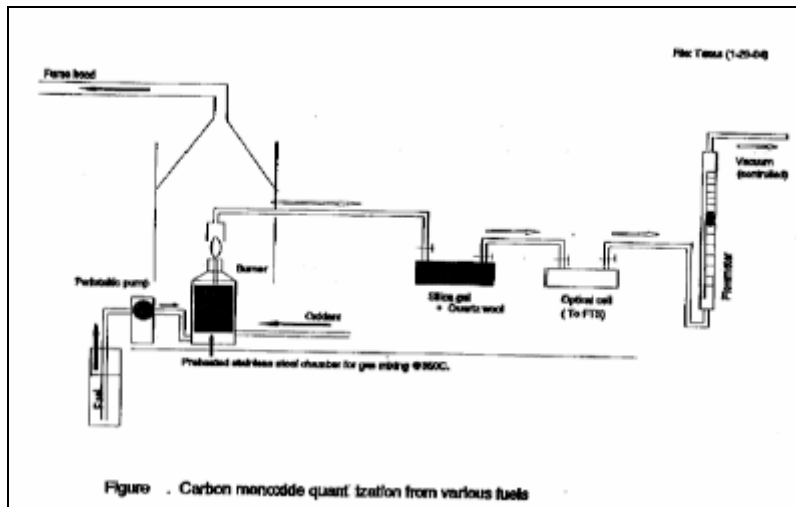
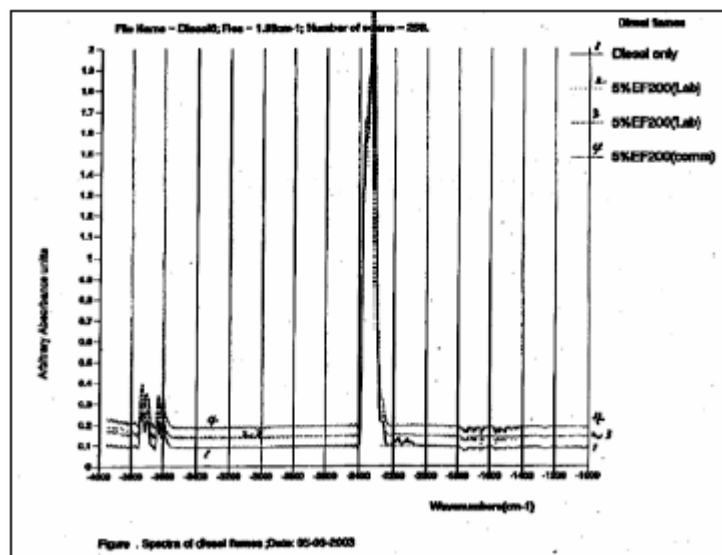


Figure 6



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Figure 7

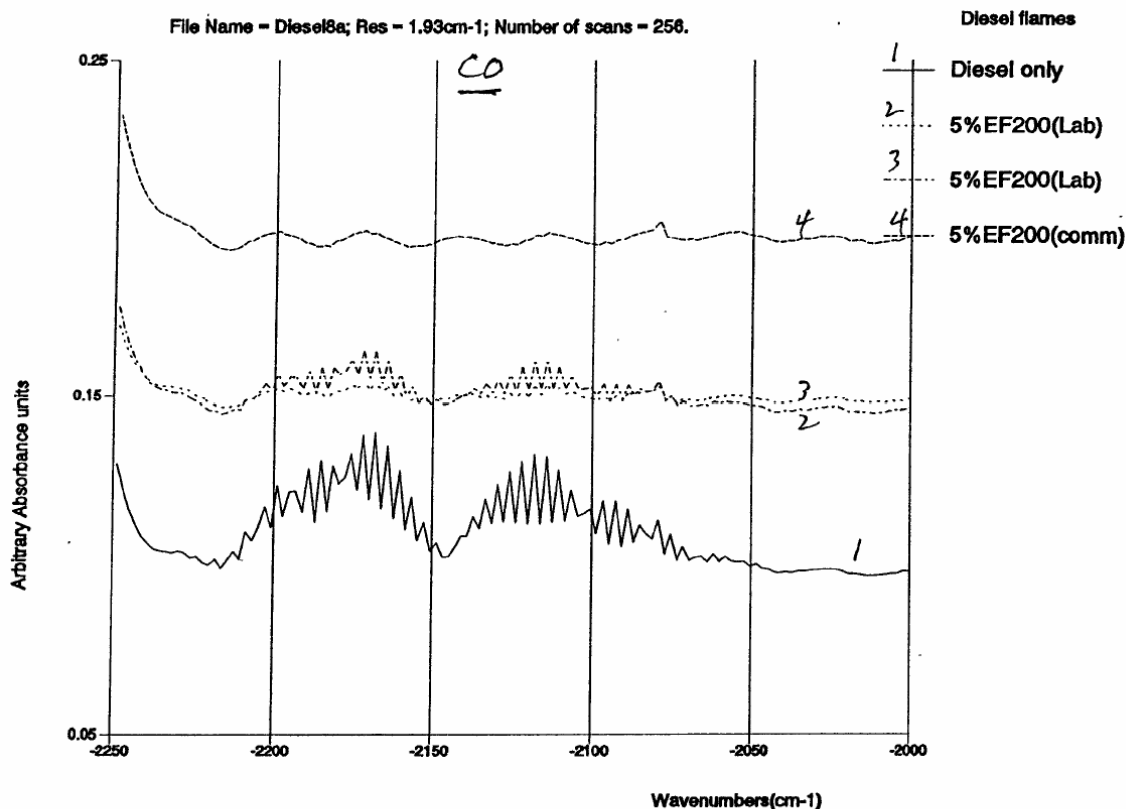
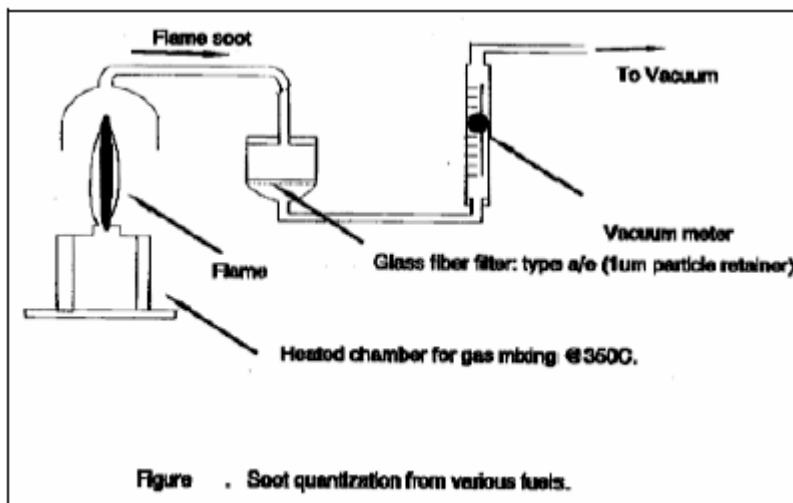


Figure . Spectra of diesel flame ;Date: 05-06-2003

Particulate Matter

Estimations of particulate emission from diesel fuel combustion were carried out by gravimetric measurement of the particles retained by 1 μ m quartz filters. A modification of the combustion apparatus (**Figure 1**), as diagrammed in **Figure 8**, enabled these measurements. In each case, the mass of a new filter was determined and subtracted from that of the filter containing particles accumulated for accurately measured periods of diesel fuel combustion time, and diesel fuel containing the additive at P levels of 15-75 ppm. For 12 individual measurements (N=12), 4 in each set, three additive formulations yielded a mean particulate reduction of 49 \pm 1% when the air/fuel ratio (A/F) in combustion was 5.5. For a lower A/F of 3.8 and the same number of measurements (N=12), the reduction in particulate averaged 55 \pm 4%. The reduction in particulate thus is somewhat dependent upon the A/F combustion ratio as well as the additive P concentration, the effects of both variables currently under investigation. This method of measurement is one of the most accurate and precise as evidenced by the low uncertainty of the results.

Figure 8



Nitrogen Oxides

Preliminary experiments demonstrated that the determination of NO_x ($\text{NO} + \text{NO}_2$) emissions using FTIR spectroscopy, as with CO, would not be possible because of the low molar absorptivity of NO in the infrared region. UV spectroscopy was used instead through monitoring the absorption by NO at 226 nm and treating the NO reduction as an index of NO_x reduction. A quartz flow cell was constructed and replaced the FTIR spectroscopic cell of **Figure 5**, at which point it was interfaced with the UV spectrophotometer having a 226 nm light source. With an additive concentration of 6 ppm and an A/F ratio of 17.8 (very lean combustion), 8 measurements ($N=8$) yielded a mean NO reduction of $25 \pm 6\%$, which we interpret as a corresponding reduction in NO_x emission.

Sulfur Dioxide

FTIR measurements were used with the apparatus and methodology of **Figure 5**, the demountable spectroscopic cell, to examine SO_2 emissions from diesel fuel containing 0.041% S. SO_2 has infrared absorption bands at 1151 cm^{-1} and 1362 cm^{-1} . The integration of the 1151 cm^{-1} band yielded estimates of SO_2 reduction from a few ($N=3$) measurements. The reduction in SO_2 was estimated from these experiments as 30%. Because of the low S content of the diesel fuel, the accuracy of these few measurements is not high and no uncertainty is attached to the value, although it is in the neighborhood of 3% SO_2 . If the mechanism of SO_2 diminution is oxidative, as the CO and particulate emissions are believed to be, a concomitant increase in SO_3 emission (and therefore sulfate), likely accompanies this SO_2 decrease. This study is to be continued with higher S fuel, but a measurable reduction in SO_2 is evident.

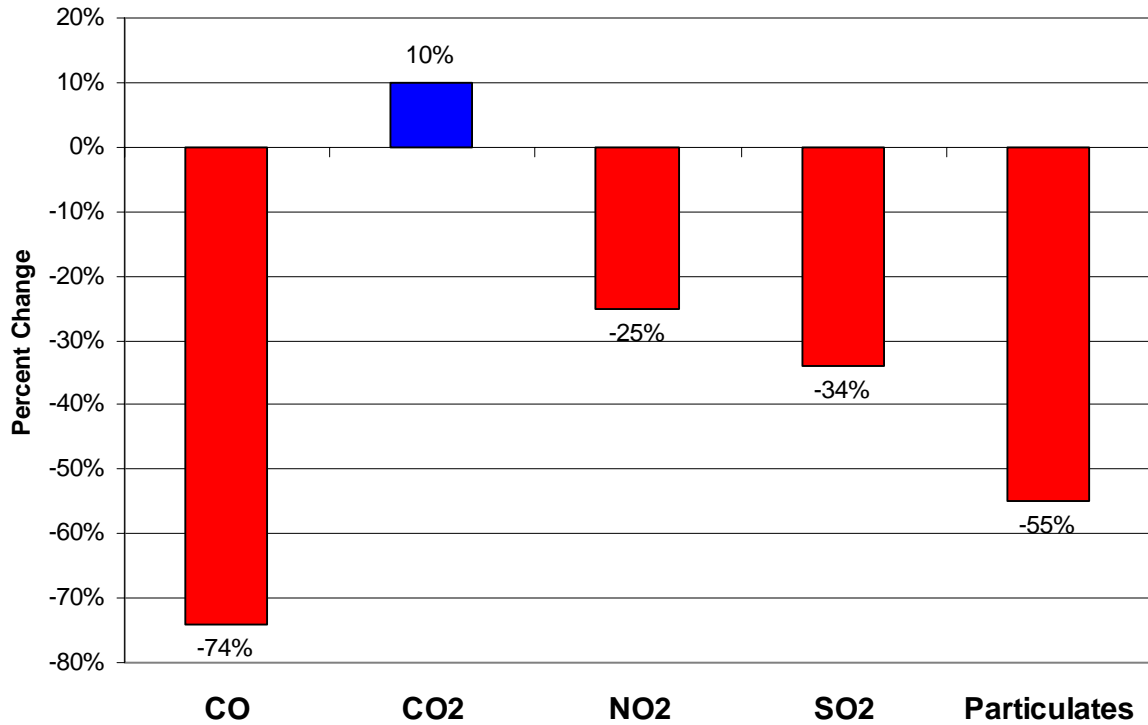
SUMMARY

Laboratory measurements show that the product DFC, when present in diesel fuel at levels of 6-17 ppm, reduces emissions of CO, particulate, NO, and SO_2 by percentages summarized in **Figure 9**. It is reasonable to assume that fuel efficiency would increase under these circumstances, concomitant with the more complete oxidation of the fuel as reflected in reduced CO and particulate. While the results of laboratory tests such as those herein described cannot

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be quantitatively extrapolated to field tests, we believe that they are indicative of emissions reduction and increased fuel efficiency that can be anticipated with the use of product DFC in hydrocarbon fuels.

Figure 9



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